PB-227 275

ANALYSIS OF THE ODOROUS COMPOUNDS IN DIESEL ENGINE EXHAUST

Arthur D. Little, Incorporated

Prepared for:

Environmental Protection Agency

June 1972

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PB 227 275

Analysis of the Odorous Compounds in Diesel Engine Exhaust

Final Report to

Coordinating Research Council

and

Environmental Protection Agency

CRC Project CAPE-7-68

EPA Contract No. 68-02-0087

for contract year ending

June 1972

Report No. ADL 73686-5

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ACKNOWLEDGMENT

It has been especially rewarding during this contract to proceed from the knowledge of the odorous diesel exhaust species to developing means for their measurement. We would like to thank the CAPE-7 Committee members whose guidance and contributions of engine and fuel technology have been especially helpful:

Dr. Roderick S. Spindt - Chairman, Gulf Research and Development
Roger C. Bascom - Cummins Engine Company
Dr. Gerald J. Barnes - General Motors Research Laboratories
Fred J. Hills - Mobil Research and Development Corporation
Dr. Ernest W. Landen - Caterpillar Tractor Company
John E. Sigsby, Jr. - Environmental Protection Agency

Mr. Timothy C. Belian's efforts on behalf of the CRC office are also gratefully acknowledged.

PROJECT TEAM

The research program at ADL has been under the overall management of Dr. Philip L. Levins. Technical direction has been provided jointly by Dr. Levins (analytical) and Mr. David A. Kendall (sensory). Miss Alegria B. Caragay and Dr. James E. Oberholtzer have assumed major responsibilities for the analytical program, and Mr. Gregory Leonardos for the sensory evaluation.

We would also like to acknowledge the technical assistance of Mr. James L. Stauffer, Mr. Rafael A. Cruz-Alvarez, and Mr. Ralph C. Steeves. Odor panel members were David A. Kendall, Gregory Leonardos, Shirley A. Raymond, Loren B. Sjöström and Frederick Sullivan.

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GLOSSARY

The following terms have been used frequently in the text and are summarized here with their definitions, for the convenience of the reader.

GC – Gas Chromatography, used for sample comparison and quantitative mass measurement.

FOE – Fuel Oil Equivalent, the quantity of exhaust species present in a sample as measured by the flame ionization detector response when compared to the response calibration with fuel oil.

HRMS – High Resolution Mass Spectrometry, used for chemical identification and quantitative mixture analysis of the oxygenate fraction.

R+DB – Rings plus Double Bonds, a representation of chemical structure type by expressing the degree of hydrogen unsaturation (see Appendix G).

LCC – Liquid Column Chromatography, used as the means of separating the paraffin, aromatic, and oxygenate fractions of the organic extract from the exhaust condensate. The procedure results in a series of fractions LCC-1, LCC-2, etc. Fractions LCC-4 and LCC-10 contain the aromatic and oxygenate exhaust odor complexes.

ALC – Analytical Liquid Chromatography, the basis for the instrumental method under development.

LCP – The paraffin fraction isolated from the preparative liquid chromatography procedure.

LCA – The aromatic (oily-kerosene) fraction isolated from the preparative liquid chromatography procedure.

LCO – The oxygenate (smoky-burnt) fraction isolated from the preparative liquid chromatography procedure.

Glossary cont...........

UV - Ultraviolet, the detection mode for the ALC method.

TIA - Total Intensity of Aroma, see Appendix B for details. Value at 1 ℓ/m^3 calculated from dose/response data.

TOE - Total Organic Extract, the total organic exhaust species isolated from the sample collection by solvent extraction.

$\mu g/\ell$ - Concentration of LCO or LCA exhaust fractions per liter of exhaust.

$mg/k\ell$ - Equal to $\mu g/\ell$.

ℓ/m^3 - Liters of exhaust or exhaust odor fraction per m^3 of air. Reciprocal of dilution.

I. SUMMARY

A. Introduction

The chemical species responsible for the major characteristics of diesel exhaust odor have been identified in the previous effort (1-3) on the CAPE-7 program sponsored jointly by the Coordinating Research Council and the Environmental Protection Agency. This report represents the beginnings of an effort to obtain appropriate means for measuring the odorous species in diesel exhaust and develop the quantitative relationships between these measurements and the exhaust odor.

Through the integrated application of analytical chemistry and sensory methods, the major odorous species have been identified. Diesel exhaust odor can be described as having two major odor groups--oily-kerosene and smoky-burnt. The oily-kerosene odors are due principally to the alkyl-substituted indans, tetralins and alkyl benzenes in the aromatic portion of the unburned hydrocarbons. The smoky-burnt character is due primarily to the partial oxidation products of these same aromatic species, plus a smaller contribution from paraffin oxidation products--specifically; alkyl, hydroxy, and/or methoxy-substituted indanones, phenols, benzaldehydes, and alkenones.

Our efforts during this past year have been to translate the large amount of detailed basic information obtained on diesel exhaust odor into a simpler base from which the final objectives could be realized.

B. Results

To obtain a more precise determination of exhaust odor intensity, new odor measurement techniques were developed in the form of a dose/response relationship. In this technique the sample odor intensity is reported by an odor panel using a dynamic test chamber and the presentation of a range of controlled concentrations. This method has allowed us to obtain data satisfactory for use in developing the quantitative odor/analytical relationships.

Knowledge of the exhaust odor chemistry has led to simpler means for the measurement of those species. Correspondingly, the sample size requirements for analysis have decreased. These results have enabled us to develop a simple, convenient means for collecting the required 500 - 1000 liter exhaust samples using Chromosorb 102 adsorbent traps at sampling rates of about 10 ℓ/min. This size sample is sufficient for the detailed odor and chemical analyses. For the proposed new analysis method, only 5 - 50 liters are required and can be collected in smaller traps at the rate of 1 ℓ/min.

A routine preparative scale liquid chromatographic procedure has been described which separates the diesel exhaust sample into its three major chemical fractions: paraffin (LCP), aromatic (LCA), and oxygenates (LCO). The LCA and LCO fractions represent the oily-kerosene and smoky-burnt odor groups. The LCP fraction does not contain species contributing to the exhaust odor.

Mass spectrometry methods have been completed for the aromatic and oxygenate fraction which enable us to compare the relative amounts of odorous components in the two isolated odor fractions. The methods involve a matrix analysis using low resolution data for the aromatics fraction and high resolution data for the oxygenate fraction.

A range of fuel and injector variables were examined using the 4-71* engine in order to generate a set of data to test odor-analytical correlations and to determine the adequacy of the available chemical data to describe the odor. The data available from the odor character definition studies did not cover a wide enough dynamic range for correlation studies.

The study included No. 1 and No. 2 diesel fuels and a paraffin fuel, and the S-60, N-60, and LSN-60 injectors. The exhaust odor intensity was the same for all conditions except for the S-60 injectors which was higher. The No. 2 fuel exhaust had new tarry character terms to modify the normal description of exhaust. The paraffin fuel exhaust was significantly different in character, best described as smoky candle-sour oxidized, although of equal intensity.

These studies have shown that the intensity of the oily-kerosene and smoky-burnt exhaust odors can be represented by the total quantity of the aromatic (LCA) and partial oxidation (LCO) exhaust fractions. Further, we have found that the total exhaust odor intensity appears to be accurately represented by the abundance of the partial oxidation products as determined by liquid chromatographic procedures.

We have begun to develop the basis for an instrumental approach to the simple measurement of the exhaust odorants based on analytical liquid chromatography procedures.

---

* Detroit Diesel Allison Division, General Motors Corporation, Model 4154N

II. BACKGROUND

This section briefly reviews the approach which was developed during our previous research on the CAPE-7 project and describes some of the methods which carry over into the research described in this report.

The main emphasis in our program is to use the sensory response of experienced odor chemists to guide and determine the effect of the various analytical procedures developed for the identification and measurement of the odorous species in diesel exhaust.

The test facility is described in detail in Appendix A. Standard operating conditions have been 1800 rpm, 33% load, N-60 injectors, and No. 1 diesel fuel. The facilities for determining the odor of exhaust or its analytical fractions are described in Appendix B.

Using the odor profile method, the exhaust produced under the standard operating conditions has been described at a 600/1 dilution as:

Total Intensity of Aroma (TIA)	2
Oily	2
Burnt	2
Kerosene	1½
Eye irritation	✓
Nose irritation	✓

(See Appendix B for Explanation of Odor Method)

Our integrated experience in the perception of diesel exhaust odor has led us to describe the odor quality and intensity in terms of two groups--oily-kerosene and smoky-burnt--each of which contributes about equally to the overall exhaust odor.

The oily-kerosene odors are due principally to the alkyl-substituted indans, tetralins and alkyl benzenes in the aromatic portion of the unburned hydrocarbons. The smoky-burnt character is due primarily to the partial oxidation products of these same aromatic species, plus a smaller contribution from paraffin oxidation products--specifically: alkyl, hydroxy, and/or methoxy-substituted indanones, phenols, benzaldehydes, and alkenones. These findings are summarized in greater detail in Appendix C.

In the earlier stages of the program, it was necessary to collect large volumes of exhaust in order to obtain sufficient quantity

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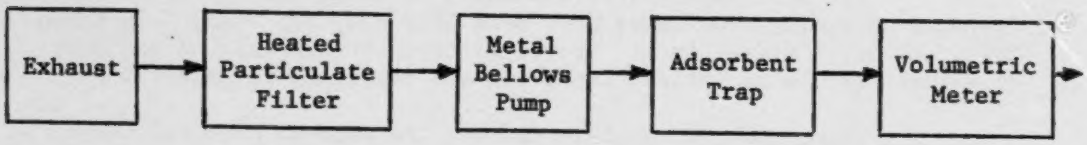
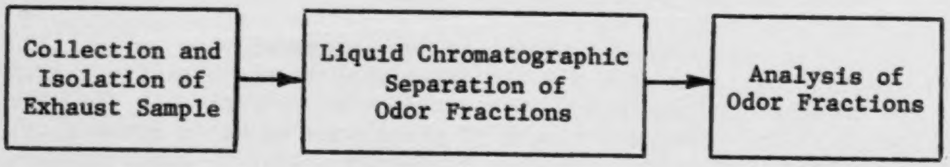
of odorous material to carry through the detailed analytical procedures required for identification of specific odorous compounds. However, now that the odorous species are known, it has been possible to develop simpler procedures for their measurement. In addition, more efficient means have been found for collection of the odorous exhaust species. The new analytical and odor procedures require 500 - 1000 liters of exhaust which are collected in the manner shown below.


Exhaust
Heated Particulate Filter
Metal Bellows Pump
Adsorbent Trap
Volumetric Meter

Silica gel was first used in the adsorbent trap, but the results in this report describe the currently preferred adsorbent, Chromosorb 102.

The exhaust isolated from the adsorbent trap by solvent elution is separated into a major paraffinic, non-odorous fraction and aromatic and oxygenate fractions containing the oily-kerosene and smoky-burnt exhaust odors respectively. This silica liquid chromatography procedure is shown schematically in Figure 1, and it is also described in detail in Appendix E. The original procedure involved the collection of eleven fractions, of which two, LCC-4 and LCC-10, contained the aromatic and oxygenate odorous materials.

In developing procedures for the analysis of the odorous exhaust species, we have followed a generalized scheme which involves


Collection and Isolation of Exhaust Sample
Liquid Chromatographic Separation of Odor Fractions
Analysis of Odor Fractions

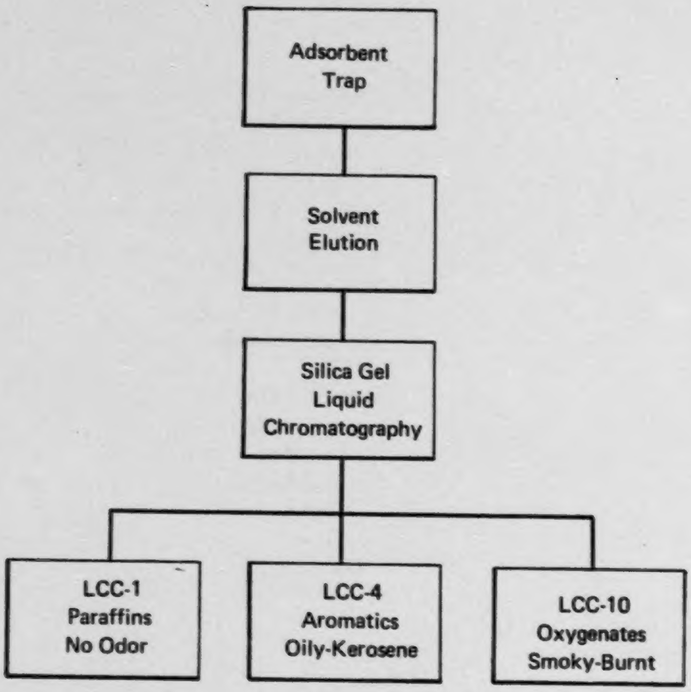

Adsorbent Trap
Solvent Elution
Silica Gel Liquid Chromatography
LCC-1 Paraffins No Odor
LCC-4 Aromatics Oily-Kerosene
LCC-10 Oxygenates Smoky-Burnt

FIGURE 1 LIQUID CHROMATOGRAPHY DIESEL EXHAUST FRACTIONATION PROCEDURE

III. CHEMICAL ANALYSIS OF ODOR FRACTIONS

Previously (3), we were able to show that a matrix analysis of the low resolution mass spectrum of the LCC-4 fraction containing the oily-kerosene odor would provide a measure of the amount of alkyl benzenes and indans/tetralins in that sample, as well as the more abundant naphthalenes. Further, an indication was obtained that the amount of indans/tetralins injected into the odor test room, as computed from the analytical data, did relate to the kerosene odor intensity. To a lesser extent, the alkyl-benzene concentration also correlated with the oily odor intensity of those fractions.

We also suggested that, although the oxygenates smoky-burnt odor fraction was much more complicated, a comparable type of analysis might be possible utilizing data obtained from the complete high resolution mass spectrum of the LCC-10 liquid chromatography fraction. It is important to remember also that we do not know with the certainty that was established for the oily-kerosene odor fraction just which groups of oxygenated species we prefer to measure to reflect the odor of that sample. Therefore, an analytical method for the oxygenate fraction should summarize chemical species concentration data where possible but leave a maximum possibility for examining the data in several combinations.

An analytical method has been developed for a detailed representation of the smoky-burnt oxygenate fraction. A detailed explanation of the analysis methods for both the aromatic and oxygenate fractions is given in Appendix G. The type of information obtained from each analysis is given in Table 1.

The aromatics analysis gives the abundance of the indans and tetralins related to the kerosene odor and the abundance of the other chemical groups in the fraction. The oxygenates analysis is a means of representing, on an internally consistent basis, the different types of chemical groups present in the fraction which were identified as odorous species. The matrix does not represent the percent abundance of these groups in the sample but does provide an efficient means of comparing samples and searching for odor significant differences. The R+DB value is a definition of chemical class based on hydrogen unsaturation, while the columns O_1, O_2, and O_3 indicate the relative amount of each class found with that number of oxygens. Thus, R+DB $1/O_1$ could be aldehydes and ketones, R+DB $2/O_1$ unsaturated aldehydes, R+DB $4/O_1$ phenols, R+DB $6/O_2$ hydroxy indanones, etc. (See Appendix G for a more complete explanation).

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Table 1

Typical Chemical Analysis Information for Odor Fractions

Composition of Aromatics Oily-Kerosene Fraction (LCC-4 or LCA)

Group	Weight %
Alkylbenzenes	62
Indans/tetralins	23
Naphthalenes	17
Acenapthenes	-
Phenanthrenes	-

Representation of Oxygenates Smoky-Burnt Fraction (LCC-10 or LCO)

R+DB	O_1	O_2	O_3
1	1	0	0
2	15	1	0
3	13	2	0
4	10	2	0
5	16	3	0
6	13	3	1
7	4	2	0
8	5	1	0

IV. SAMPLE COLLECTION

A. Trapping

Previous studies (3) have shown that silica gel adsorbent traps were a much more efficient means of collecting the odorous components in diesel exhaust than the condensation methods. Further studies were conducted to quantitatively define the performance of these traps. We found that their efficiency was particularly susceptible to the water content in the exhaust, and this factor limited the utility of silica gel. Experiments were then conducted with two Johns-Manville Chromosorb adsorbents.

Chromosorb 101 and 102 are crosslinked polystyrene porous adsorbents frequently used in gas chromatography studies. They were attractive for our purposes because, like charcoal, they would have low water retention but also had a higher probability of quantitative sample recovery. In previous studies with charcoal we had been unable to recover the odorous fractions of exhaust. Chromosorb was also shown to be effective in the IIT Research Institute (5) diesel odor program.

Comparison of the Chromosorb 101 and 102 which have, respectively, surface areas of 15 - 30 m^2/g and 300 - 400 m^2/g showed that the Chromosorb 102 had the greatest overall efficiency. Exhaust samples were collected by the scheme diagrammed in "Background" using stainless steel collection tubes and the procedures described in Appendix D. The overall collection efficiency of the Chromosorb 102 traps can be seen in Figure 2 where total hydrocarbons were monitored at the entrance and exit from the trap. No odor was observed to penetrate the trap. We believe that the 30 - 40 ppm C level out of the trap represents the light ends, CH_4, etc., of the exhaust hydrocarbons. We have designated samples collected using the Chromosorb procedure by a number preceded by the code CHROM.

B. Extraction

The sample is extracted from the Chromosorb bed by backflowing solvent through the trap. Using this method, studies have been conducted to determine the optimum solvent volume for extracting the exhaust components from the Chromosorb. The data are summarized in Table 2 for 1000-liter collections of exhaust under standard engine operating conditions. By maintaining the solvent flow through the adsorbent bed at 0.5 mℓ per minute, the trapped sample is virtually totally eluted in the first 10 mℓ of pentane. Only negligible amounts of material are further extracted with more pentane and with the more polar methylene chloride.

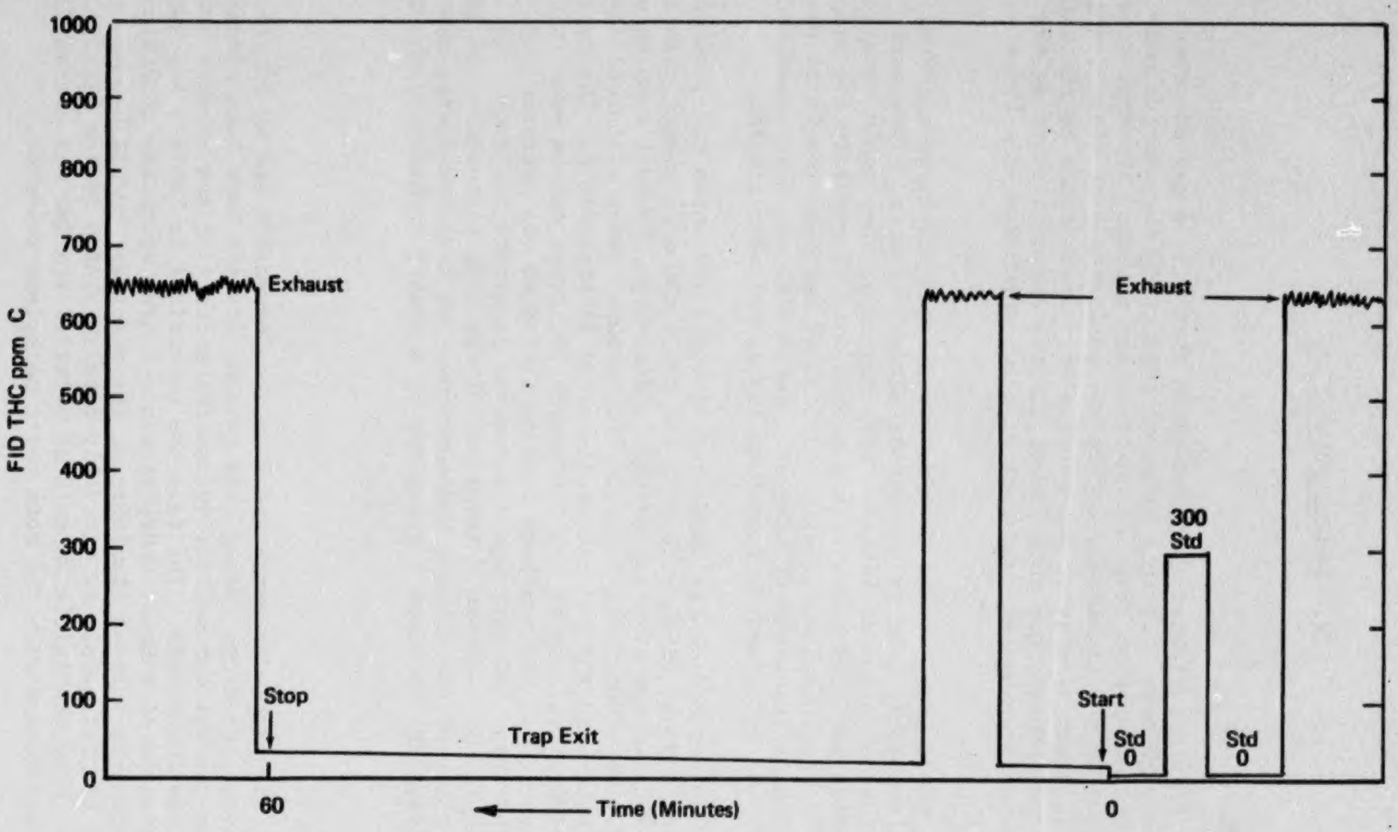

FIGURE 2 CHROMOSORB 102 TOTAL HYDROCARBON TRAPPING EFFICIENCY

TABLE 2

Extraction of Diesel Exhaust Samples from Chromosorb 102

	mg/Kℓ of Exhaust Extracted from Various Samples[(a)]			
Solvent Sequence	Chrom. 32	Chrom. 33	Chrom. 34[(b)]	Chrom. 35
Pentane, 10 ml	260.0	223.0	231.0	236.0
Pentane, 10 ml	1.8	1.4	2.0	1.7[(d)]
Pentane, 25 ml	1.3	0.7	1.1	-
CH_2Cl_2, 50 ml	(c)	(c)	(c)	0.7[(e)]

(a) Represents a collection of 1000 ℓ from an engine operating at 33% load with No. 1 Diesel Fuel and N-60 injectors.

(b) Represents a collection of 600 ℓ.

(c) No detectable material observed.

(d) 50 mℓ of pentane extract.

(e) 10 mℓ of CH_2Cl_2 extract.

Each solvent extract has been evaluated for odor characteristics on blotter strips. The results of these analyses consistently show that all the characteristic odor of diesel exhaust is concentrated in the first 10 mℓ of pentane. The other fractions do not have any recognizable odor.

C. Analytical and Odor Results

A comparison of the composition of the diesel exhaust samples collected by various sampling methods is summarized in Table 3. All samples were collected under the standard engine operating conditions. The total organic extracts (TOE) of the samples collected by aqueous condensation, which we have reported before (3) to be equivalent to only about 10% of the total exhaust odor, is also only 10% of the total organic extract compared to the silica gel and the Chromosorb 102 samples. The data also suggest an expected preferential trapping of the oxygenated compounds in the aqueous condensate. The silica gel traps suffer by comparison in the apparent loss of aromatics. Both Chromosorb 101 and 102 appear to trap the aromatics and oxygenated compounds efficiently and equally, but as reported earlier, the Chromosorb 101 showed early breakthrough of hydrocarbons and, therefore, provided less margin of safety.

The samples collected on the Chromosorb 102 were subjected to the standard liquid chromatography (LCC) fractionation and examined in the odor test room (See Appendix B for procedure). The results of this work are summarized in Table 4. The detailed odor profiles are listed in Table 5, and the mass spectrometry analyses of selected aromatic and oxygenated fractions are given in Table 6. (See Appendix G for details on analysis procedure).

The reproducibility of the LCC-4 and LCC-10 oily-kerosene and smoky-burnt odor fractions is quite encouraging and appears to be within the measurement error. The sensory evaluation of the two intense odor fractions, TOE and LCC-10, is similar for all samples, but the LCC-4 fraction shows some variation. We believe that in part the variability observed is due to use of the static test room facility as previously reported. Results reported in Section VI demonstrate the value of the dynamic test chamber for such observations and a greater reproducibility in results.

Table 6 summarizes the detailed analyses of the odor-containing fractions. The aromatics fractions of the diesel exhaust samples show a composition similar to that of the No. 1 fuel. (These results should be taken on a comparative basis only, because of periodic changes in the spectrometer calibration.) The oxygenate analysis of the LCC-10 fractions for Samples Chrom 32 and Chrom 33 shows a remarkably good agreement.

TABLE 3

Comparison of Diesel Exhaust[(a)] Collected by Various Sampling Techniques

(Concentrations in mg/Kℓ)[(b)]

Sampling Method	TOE	LCC 4	LCC 10
Aqueous Condensate	23	4.0 (20%)	2.7 (14%)
Gel	240	13.0 (6%)	7.3 (3%)
Chromosorb 101	138	36.4 (28%)	6.5 (5%)
Chromosorb 102	258	38.2 (15%)	5.7 (2%)[(c)]

---

a. Engine conditions - 33% load, No. 1 Diesel Fuel, N-60 injector.

b. All values derived from GC data described in Appendix F.

c. This value is slightly lower than the other LCC-10 fractions by an amount equivalent to the oxygenated compounds that elute in earlier fractions in the methylene chloride system (see Section V)

TABLE 4

Summary Chromosorb 102 Analytical and Odor Data

	TOE		LCC-4[a]		LCC-10[a]	
CHROM	Mg/Kℓ	TIA[b]	Mg/Kℓ	TIA[b]	Mg/Kℓ	TIA[b]
28	259	1½-2	36	?	5.0	1-1½
29	316	2	39	½	7.6	1
30	260	2	-	-	-	-
31	270	1½	-	-	-	-
32	260	1½-2	38	?	4.5	1½
33(c)	223	-	38	1	6.4	-
34	231	-	40	-	5.0	-
Avg	258	1½-2	38	½	5.7	1½

(a) Using methylene chloride LCC elution modification (see Section V).

(b) 21 ℓ aliquot in odor test room, 600/1 dilution.

(c) Three fraction routine separation; LCP, LCA, LCO (see Appendix A).

TABLE 5 : STATIC TEST ROOM ODOR OF CHROMOSORB SAMPLES

	Chrom 27	Chrom 28	Chrom 29	Chrom 30	Chrom 31	Chrom 32	Chrom 33
TOE 600/1[a]		TIA 1½-2 Smoky sooty 1½-2 Ox. oily 1½ Naphthanate 1 Kerosene)(Eye ✓ Nose ✓	TIA 2 Smoky 2 Naphthanate 1½ Ox. oily 1 Kerosene Eye ✓ Nose ✓	TIA 2 Burnt smoky 1½-2 Naphthanate 1 Ox. oily 1½ Kerosene ? Nose irr. ✓ Particles ✓	TIA 1½ Smoky 1 Naphthanate 1-1½ Ox. oily 1 Nose irr. ✓ Particles ✓	TIA 1½-2 Burnt smoky 1½ Ox. oily sour 1½ Naphthanate 1 Kerosene ½ Nose irr. ✓	
LCC-4 600/1	TIA 1 Oily ½-1 Musty ½	?Fuel related	TIA ½ Naphthanate)((Woody musty) Oily)(Smoky ?			?Fuel related	LCC Ar. TIA 1 Woody musty naph. 1 Oily ½ Nose irr. ✓ Fullness ✓
LCC-4 300/1		TIA ½ Musty pungent ½ Ox. oily)(	TIA ½ Musty naph.)(-½ Oily)(Smoky ?				
LCC-10 600/1	TIA 1½ Smoky 1½ Ox. oily 1 Musty Naph. 1 Nose Irr. ✓	TIA 1-1½ Musty Naph. 1-1½ Smoky sooty ½ Ox.oily ½-1 Nose irr. ✓ Solventy ?	TIA 1 Musty smoky 1 Particulate ✓ Ox. oily ½ Nose irr. ✓			TIA 1-1½ Burnt smoky 1 Ox. oily 1 Naphthanate 1 Nose irr. ✓	

a. Dilution in test room

TABLE 6

Chromosorb 102 Detailed Odor Fraction Mass Spectrometric Analyses[a]

Aromatics Analysis

% Relative Composition

	Chrom 33 LCA	Chrom 34 LCC-4	No. 1 Fuel
Alkyl Benzenes	62	57	57
Indans/Tetralins	23	26	27
Naphthalenes	17	19	18

Oxygenate R+DB Analysis

% Relative Abundance

	Chrom 32 LCC-10			Chrom 33 LCO			Chrom 34 LCC-10		
R+DB	O_1	O_2	O_3	O_1	O_2	O_3	O_1	O_2	O_3
1	0	0	0	1	0	0	0	0	0
2	16	2	0	15	1	0	13	2	0
3	20	3	0	13	2	0	18	3	0
4	13	3	0	10	2	0	13	3	0
5	9	4	0	16	3	0	9	4	0
6	11	5	0	13	3	1	14	5	1
7	3	2	0	4	2	0	4	2	0
8	0	2	0	5	1	0	0	2	0

a. See Appendix G for details of analysis

V. LIQUID CHROMATOGRAPHY

A. Methylene Chloride Modification

The standard liquid chromatography procedure used earlier in our research (Appendix E-1) had several disadvantages. The solvent choices for the gradient elution were more complex than necessary for the separation, and the hexane used was frequently found to contain higher aromatic impurities. Also, benzene absorbed strongly in the ultraviolet spectrum and prevented us from developing simpler analysis methods based on UV spectrophotometry with this solvent.

Accordingly, the normal procedure was modified to a smaller scale to match the new analytical requirements, and a simpler solvent gradient was developed using the series pentane, methylene chloride, and 10% methanol in methylene chloride. The procedure is described in detail in Appendix E-2.

This solvent system gives sample resolution comparable to that of the former method in that the paraffins which constitute the main bulk of the sample still elute in fraction LCC-1, the aromatics in fraction LCC-4, and the oxygenates in fraction LCC-10.

The results of a typical separation using this scheme are shown in Table 7. The data shown represents the fractionation of a diesel exhaust sample (Chrom 32) from the collection of 1000 liters of exhaust on Chromosorb 102. The diesel engine was operated under standard conditions.

The values noted are closely analogous to our previously reported data (3) using the benzene solvent gradient. Note that the LCC-3 fraction contains a slightly higher mass than the preceding fraction indicating partial elution of the aromatics. Indeed, UV analysis of this fraction at 254 nm shows the presence of UV absorbers indicative of aromatic compounds. There is also some mass observed in fractions LCC-5 to LCC-8 which was not observed in the benzene solvent gradient.

Blotter strip odor evaluation of each of these fractions revealed no odor for fractions LCC-1 and LCC-2, a trace of oily-kerosene in fraction LCC-3 with most of that characteristic odor note in fraction LCC-4. Fraction LCC-10 contained the smoky-burnt odor notes. The intervening fractions contained the oxidized-oily notes that at times have also been observed in corresponding fractions in experimental gradient systems.

In order to determine the composition of the species eluting in fractions LCC-5-8, a high resolution mass spectrometric analysis was

TABLE 7

Methylene Chloride LCC[a] Elution Scheme for Diesel Exhaust Sample CHROM 32[b]

LCC Fraction	Solvent and Effluent Volume	mg/Kℓ[c] of Exhaust	
1	Pentane, 5.0 mℓ	201.0	Paraffins
2	Pentane, 3.0	1.3	
3	Pentane, 3.0	12.1	
4	CH_2Cl_2, 5.0	37.7	Aromatics
5	CH_2Cl_2, 2.5	0.3	Aldehydes and Ketones
6	CH_2Cl_2, 2.5	0.2	
7	CH_2Cl_2, 5.0	0.5	
8	10%MeOH/CH_2Cl_2, 2.5	0.2	
9	10%MeOH/CH_2Cl_2, 2.5	---	
10	10%MeOH/CH_2Cl_2, 2.0	4.5	Oxygenates

(a) On micro-column of activated silica Grade 950, 0.6 cm x 12 cm The column volume is 2.1 mℓ.

(b) Engine operating conditions - 33% load, No. 1 diesel fuel, N-60 injector.

(c) Based on GC analysis of each fraction on 1 1/2' x 1/8" 10% OV-1 column.

made on fraction LCC-5 from sample CHROM-27, which contained sufficient material for analysis. The species observed and their relative abundance are listed in Table 8. After examination of the entire spectrum, it appears that most of these species are aldehydes and ketones as follows:

R+DB 5	Benzaldehydes
R+DB 6	Indanone
R+DB 8	Naphthaldehydes

The R+DB matrix presentation of this fraction is shown in Table 9. The indication from this sample is that oxidized-oily odor notes are represented at least in part by R+DB 5/O_1 and perhaps to some extent by the O_1 R+DB 6 and 8 groups.

B. Routine Preparative Liquid Chromatography Procedure

The liquid chromatographic separation of the primary diesel exhaust fractions has been simplified so that a routine procedure could be described for isolation of the two odor fractions. Since the exhaust species consist only of the paraffin, aromatic, and oxygenate components, a simple procedure would give rise to only these three fractions--rather than the 10-12 fractions normally collected in the LCC procedures used to date.

Such a procedure has been developed and is described in detail in Appendix E-3. Typical results using this method are shown in Table 10. The silica column is as used in the normal LCC procedure. The gradient consists of three solvents added in the order and volumes shown. Three fractions containing the paraffins (LCP), aromatics (LCA), and oxygenates (LCO) are collected.

Odor evaluation of these fractions reveals no odor in LCP, the oily-kerosene odor in LCA, and the smoky-burnt odor in LCO. Mass spectral analysis of the LCA and LCO fractions gives results comparable to those of LCC-4 and LCC-10 fractions as described in the preceding section. Average mass results for LCC-4 and LCC-10 were 38 mg/kℓ and 5.7 mg/kℓ respectively, while the LCA and LCO fractions analyzed for 38 mg/kℓ and 6.4 mg/kℓ.

TABLE 8

Major Species Observed in CHROM-27 LCC-5

	% Abundance[a]	MW	C	H	O	
R+DB 5						
	14	106.0403	7	6	1	
	38	134.0718	9	10	1	
	5	148.0877	10	12	1	
	2	162.1036	11	14	1	
R+DB 6						
	2	118.0417	8	6	1	(132 fragment)
	8	132.0564	9	8	1	
R+DB 8						
	3	156.0564	11	8	1	
	4	170.0726	12	10	1	

a. Ions greater than 1% abundance

TABLE 9

R+DB Oxygenate Analysis of CHROM-27 LCC-5

R+DB	O_1	O_2	O_3
1	0	0	0
2	3	0	0
3	1	0	0
4	1	0	0
5	61	3	0
6	15	2	0
7	2	0	2
8	8	0	0

Table 10

Preparative Liquid Chromatography of Diesel Exhaust Sample Chrom 33[(b)]

Fraction[(c)]	Solvent	mg/kℓ of Exhaust Present
LCP	Pentane, 20 mℓ	165.0
LCA	CH_2Cl_2, 10 mℓ	38.5
LCO	50% $MeOH/CH_2Cl_2$, 10 mℓ	6.4

(a) Column of activated silica Grade 950, 1.1 cm x 12 cm. Column volume = 4.5 ml. (See Appendix E-3)

(b) Engine operating conditions = 33% load, No. 1 diesel fuel, N-60 injector.

(c) P - Paraffins, A - Aromatics, O - Oxygenates.

VI. DOSE/RESPONSE MEASUREMENT OF ODOR INTENSITY

As we began to explore quantitative relationships between the analytical measures of exhaust fractions and odor intensity, a careful review was made of all of the available odor data. The summation revealed that virtually all of the odor data fell in the range of TIA = 1.25 ± 0.25. Clearly, this range is too narrow to test the validity of correlations which we had developed. Most of the data had been obtained when the emphasis was still primarily on qualitative odor descriptions of exhaust and its analytical fractions. It was felt that the precision of the odor data may have been unnecessarily restricted due to observing a single concentration in the static test room. Preliminary studies in the static chamber showed that the precision of the odor measurement could be improved by observing the odor intensity at a series of controlled dilutions covering a wide dynamic range.

As a result of the success of these and subsequent experiments, this method of presenting a series of doses and measuring the odor response has been used routinely to describe the odor intensity of exhaust fractions. These measurements are carried out in a dynamic odor chamber which has been described in detail in Appendix B. This facility was constructed under programs carried out jointly for the Manufacturing Chemists Association and the Environmental Protection Agency. The primary purpose of the chamber is to instrumentally measure the involuntary physiological response to odorants. For this study, we have used only the sample presentation portions of the facility, relying on the normal panel member response to record odor intensity and character.

Typical results using this approach for the LCA and LCO oily-kerosene and smoky-burnt odor fractions are listed in Table 11 and are shown graphically in Figures 3 and 4. Using this approach, the odor intensity of these fractions is described as

$$\text{TIA (LCA)} = 1.45 + 1.35 \log (C_{LCA})$$

$$\text{TIA (LCO)} = 2.07 + 1.80 \log (C_{LCO})$$

where C is in ℓ/m^3

Table 11

Dynamic Odor Test Chamber Results - CHROM 33 Odor Fractions

Concentration (ℓ/m^3)[a]	TIA (Ave.) LCA[b]	TIA (Ave.) LCO[c]
0.8	1.25	1.5
0.05	0	0.25
0.1	0	0
0.2	0.75	1.0
0.4	1.0	1.5
0.8	1.5	1.5
0.4	0.5	1.25
0.8	1.25	1.75
1.6	1.5	2.5
3.2	2.25	3.0
6.4	2.5	3.0

a. Concentration of exhaust fraction in the odorized air.

b. Average of five panel members, ± 0.25.

c. Average of four panel members, ± 0.25.

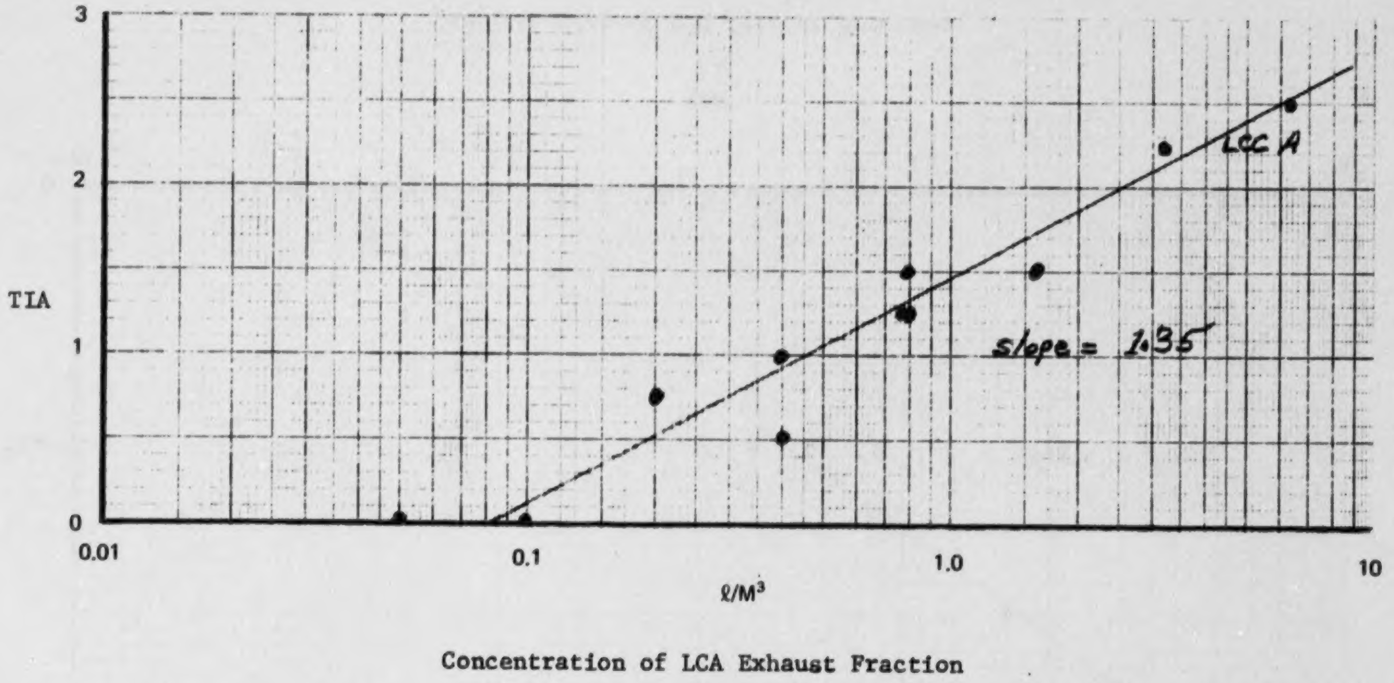

Figure 3: DOSE/RESPONSE DATA FOR CHROM 33 LCA ODOR FRACTION

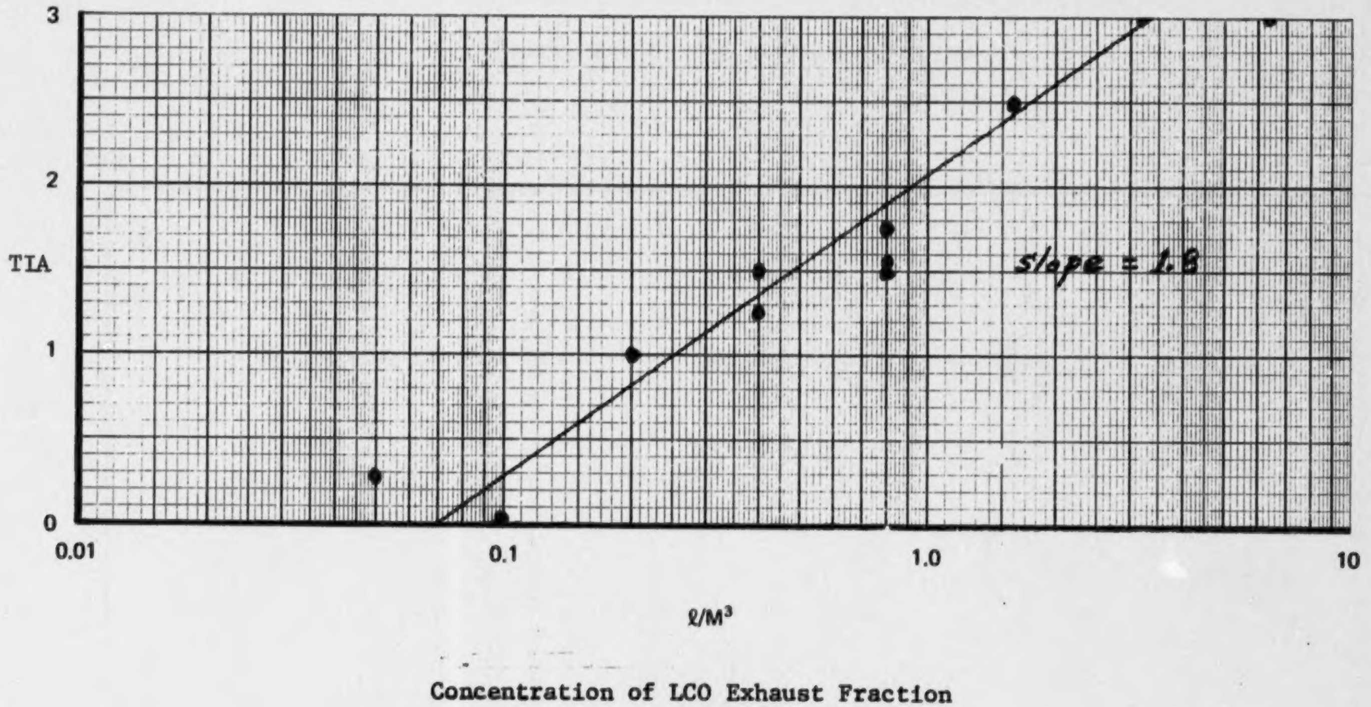

Figure 4: DOSE/RESPONSE DATA FOR CHROM 33 LCO ODOR FRACTION

The constants and slopes of the least squares lines are thus sufficient to describe the intensity of any particular sample. Statistical analysis of a large set of data obtained in this manner revealed an odor predictability of ± 0.4 TIA within 95% confidence limits (σ = 0.2 TIA). These procedures have enabled us to describe odor intensity more precisely than the older methods.

For the study of exhaust samples, the dose/response data were obtained using the static test room, which is adjacent to the engine facility.

VII. DEVELOPMENT OF A SIMPLIFIED ANALYTICAL METHOD

A. Method Development

The basis for a simple, routine method for the analysis of the odorous fractions present in diesel exhaust has been developed. The method is based on modern analytical liquid chromatographic (ALC) methods using ultraviolet detection. In preliminary studies, we found that the mass of the LCA and LCO fractions could be measured by ultraviolet spectroscopy using the correlation between their ultraviolet absorbance at 254 nm and their mass as determined by the GC method.

The method is based on the use of newly available commercial components assembled as shown schematically in Figure 5. The following components are used:

1). Two solvent reservoirs

2). Positive displacement pump (Milton Roy-Milroyal Model HDB-1-30R)

3). A silicon septum sealed injector

4). A 30 cm x 0.6 cm O.D. glass column packed with a silica gel type support - Corasil II (Waters Associates, 37-50 microns)

5). Ultraviolet absorbence detector and amplifier, detecting wavelength 254 nm (Laboratory Data Control Model 1205)

6). Recorder (a Hewlett-Packard X-Y recorder Model 7030A was available and was used with the time base).

The unit operates essentially the same as a gas chromatograph, except in the liquid phase. A solvent flow is established through the column (we have used 1 mℓ/min in most of our work). A sample is injected with a syringe, and the separated components, which absorb ultraviolet light at 254 nm, are recorded as they elute from the column. To achieve the proper elution and detection, several factors were considered. The first was that a solvent gradient was needed to resolve the odor groups,

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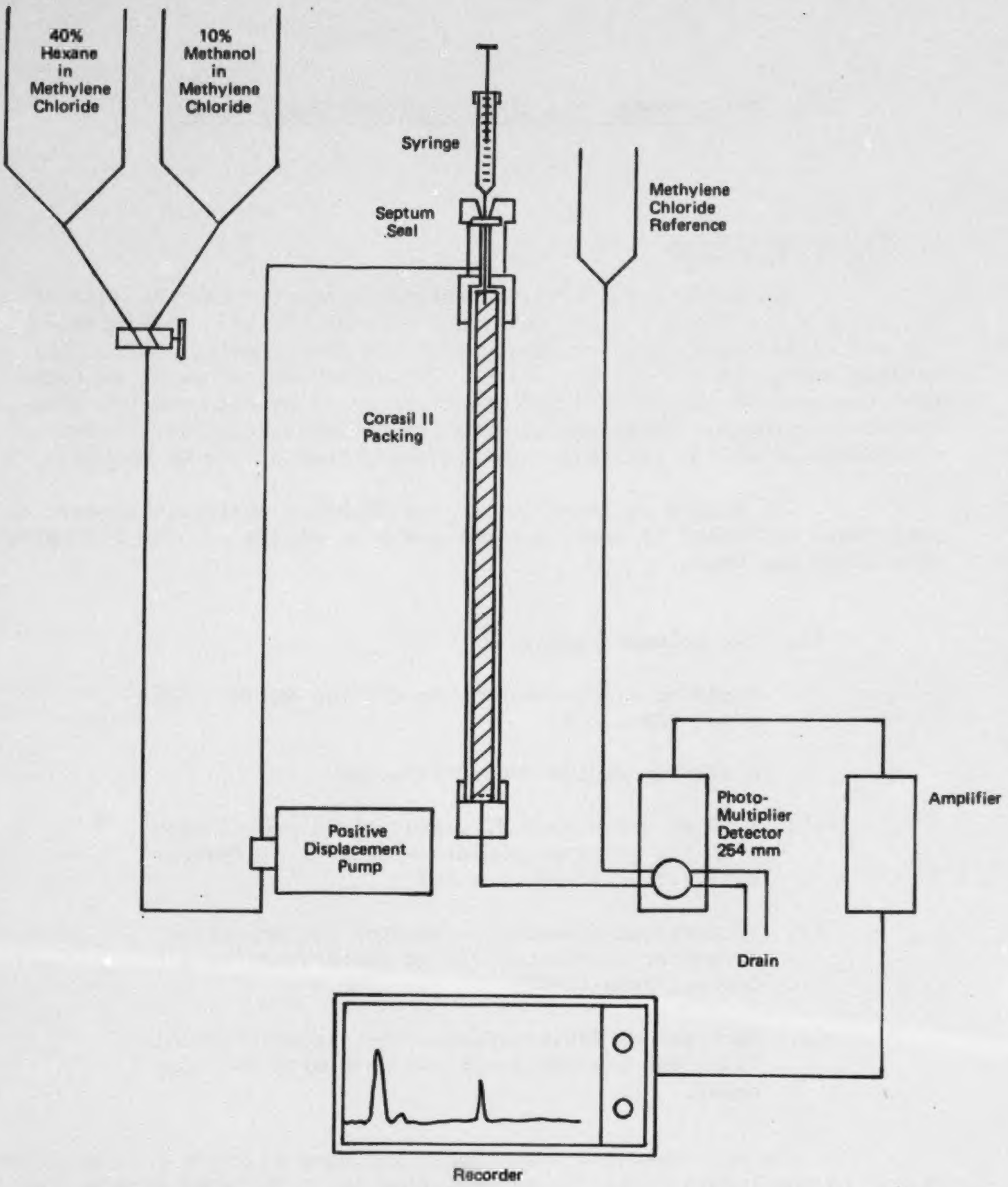
40% Hexane in Methylene Chloride
10% Methanol in Methylene Chloride
Syringe
Septum Seal
Methylene Chloride Reference
Corasil II Packing
Photo-Multiplier Detector 254 mm
Amplifier
Positive Displacement Pump
Drain
Recorder

Figure 5 **ANALYTICAL LIQUID CHROMATOGRAPH SCHEMATIC**

and the second was that the paraffin fraction did not absorb UV at any wavelength above 240 nm. Thus, an elution scheme which would allow the paraffins and aromatics to elute as a group would only record the aromatic portion. Therefore, a two-step sequence (vs. three) could be developed which required only a separation of aromatics (plus paraffins and oxygenates).

The procedure finally developed is as follows:

1). Condition column with 40% hexane in methylene chloride at a flow rate of 1.0 mℓ/min for at least 15 minutes.

2). Inject 1 - 10 μℓ of sample (containing 0.1 - 10 ℓ of exhaust fraction.)

3). After 1 minute, switch solvent selection valve to allow 1 mℓ of 10% methanol in methylene chloride to enter solvent stream and then switch back to the 40% hexane solution.

The results obtained on the TOE of sample CHROM 33 are shown in Figure 6. Peak 1 corresponds to the aromatics portion (LCC-4 or LCA) of the sample while peaks 2 and 3 correspond to LCO. In this system, using methylene chloride as an eluent, the oxygenate fraction is partially resolved into the two components as discussed earlier in Section V. Peak 2 contains the aromatic aldehydes and ketones, while peak 3 contains the more polar species. The elution volume of peak 3 represents the time required for the injected slug of methanol to equilibrate with the column and elute while displacing the polar oxygenated components. The paraffins are, as discussed, transparent to the 254 nm UV and not observed while eluting coincidentally with the aromatics in peak 1.

Confirmation of the peak assignments can be seen in Figures 7-9 which show the analysis of the LCP, LCA, and LCO fractions isolated using the preparative liquid chromatography procedure. The paraffin, fraction LCP (Figure 7), shows no UV absorbance; fraction LCA (figure 8) contains the aromatics; and fraction LCO (Figure 9) contains the total oxygenates.

At times a trace component elutes in the region of peak No. 3 due to septum and solvent background. This is considerably minimized by using only distilled solvents and conditioning septa. In the instances when this background peak is observed, the quantity of peak No. 3 is adjusted accordingly.

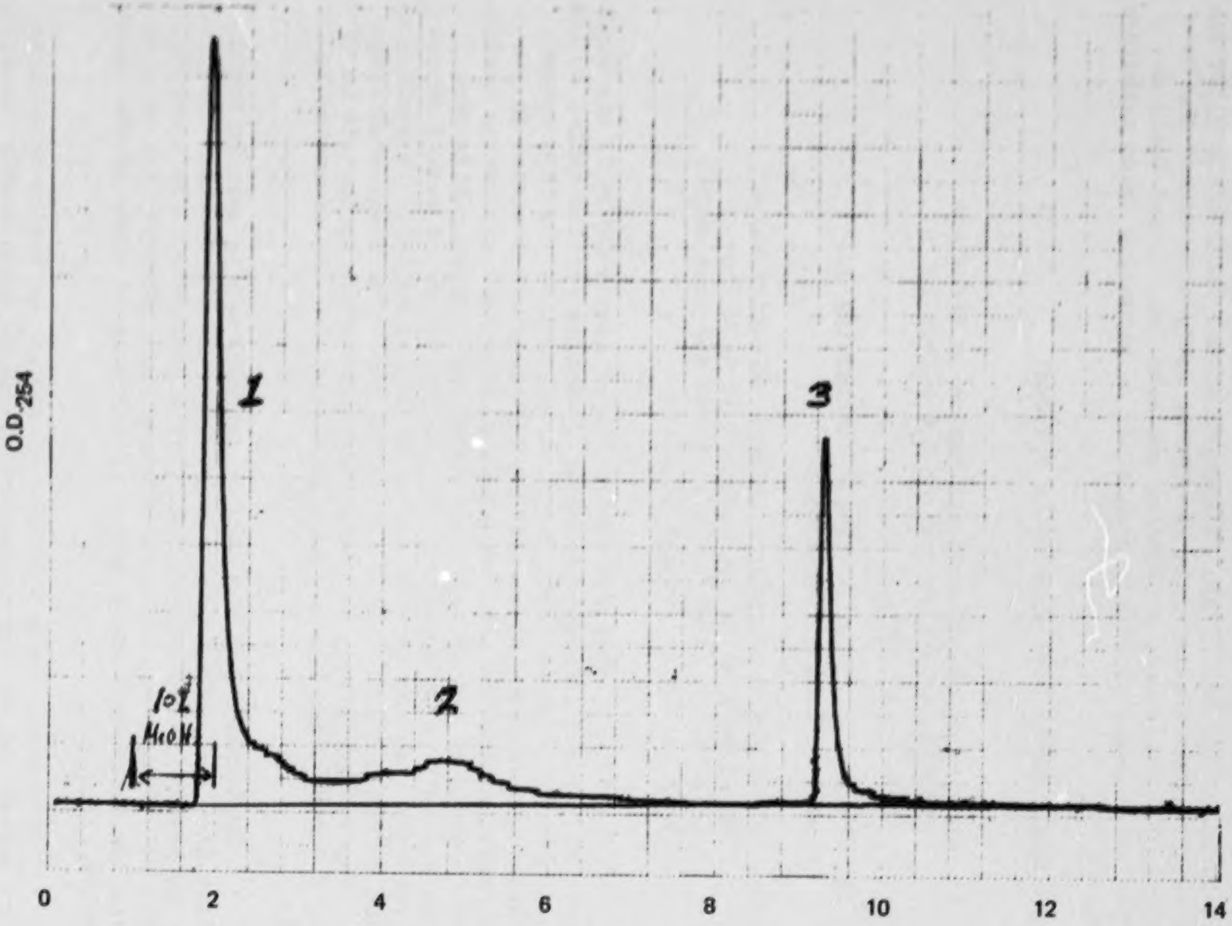

FIGURE 6 ALC OF CHROM 33 – TOE, 0.4ℓ

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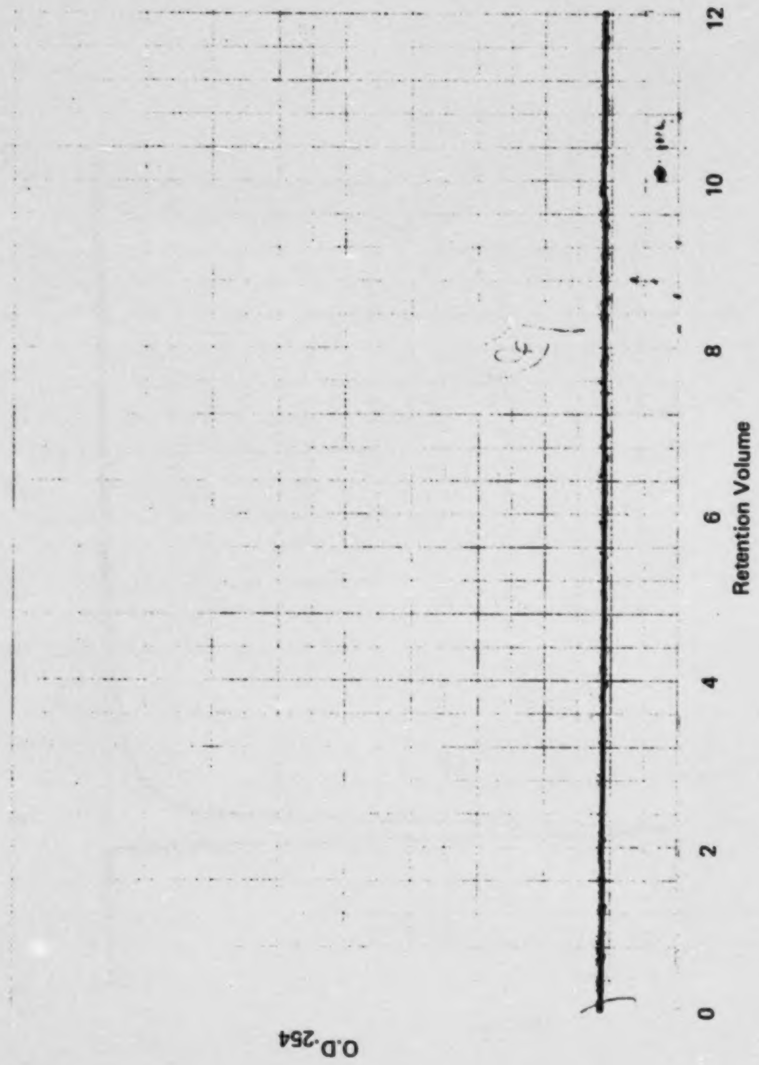

FIGURE 7 ALC OF CHROM 33 — LCP, 0.75ℓ

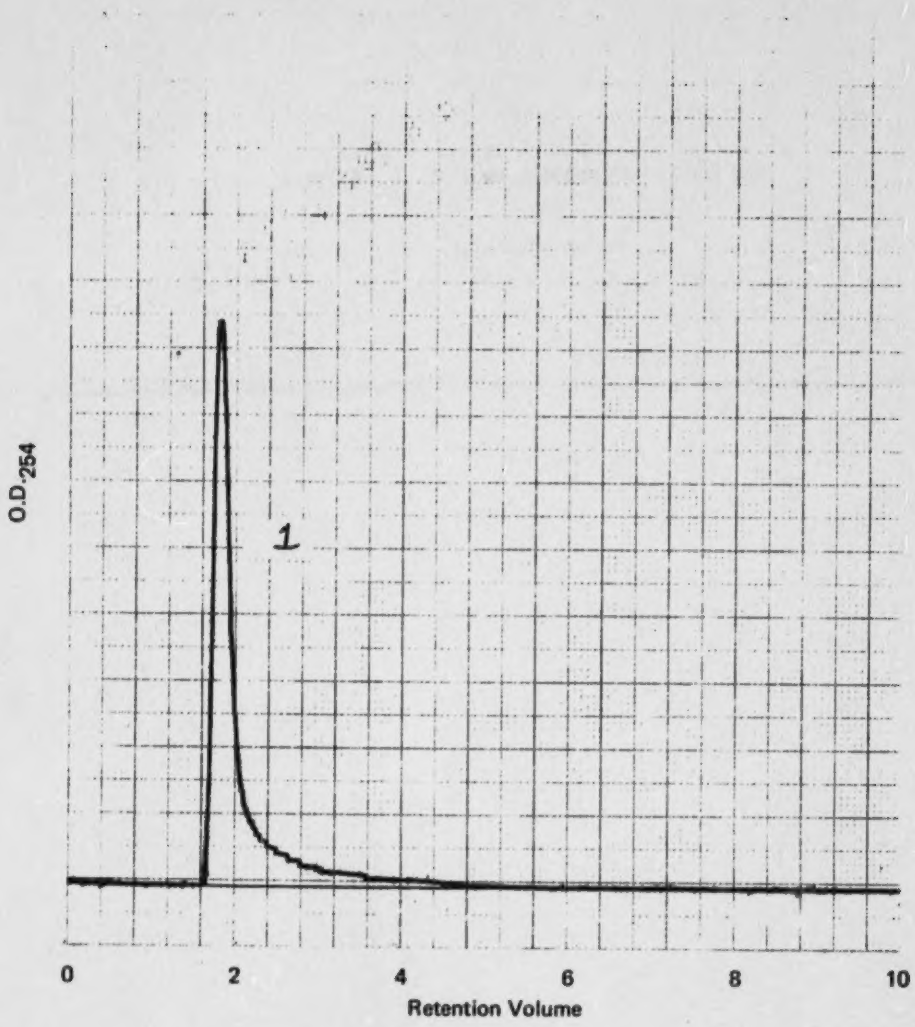

FIGURE 8 ALC OF CHROM 33 – LCA, 0.36ℓ

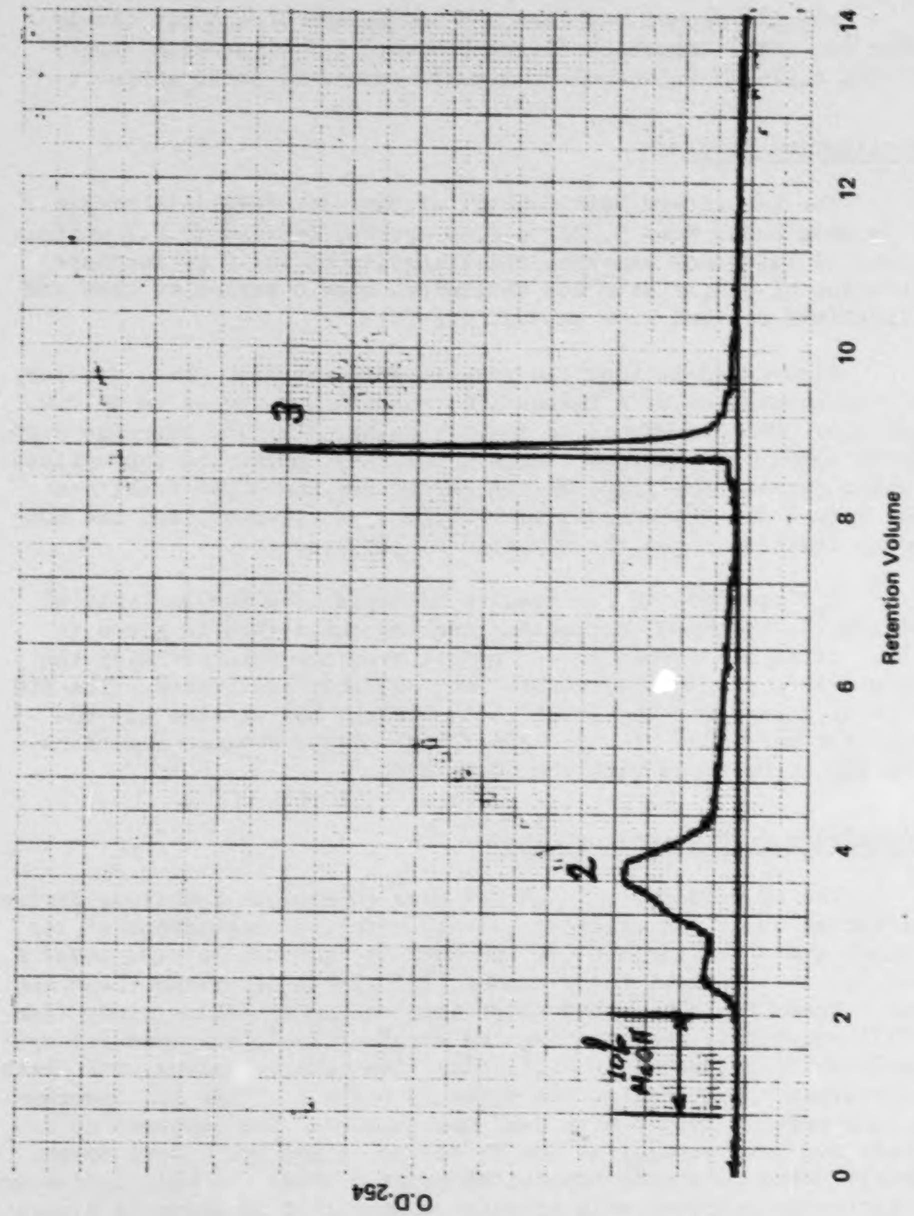

FIGURE 9 ALC OF CHROM 33 LCO, 0.75ℓ

The ALC method represents a unique way of quantitatively measuring the total aromatics (oily-kerosene) and oxygenates (smoky-burnt) from a single injection of a small amount of total exhaust.

B. Quantitative Response

The Laboratory Data Control ultraviolet (UV) detector is linear in absorbance from 0.002 to 0.64 optical density (O.D.) units. Using several reference samples, the linearity of the O.D. response as a function of sample size was determined over a period of time and using fractions derived from exhaust and fuel.

Figures 10-12 show the results obtained from these studies. Each of the samples shows a linear O.D. response vs. µg up to an O.D. of about 0.5. One can expect to readily relate the O.D. response from an exhaust sample to the odor fraction quantity, given the appropriate calibration curve. The slope of the curves for the LCC-4 fractions from No. 1 fuel and its exhaust are similar, as expected, and the LCC-10 exhaust fraction shows the expected higher response.

A comparison of the results obtained from the analysis of several samples by the GC method and the new ALC method is given in Table 12. It is clear that the UV method provides data matching the GC data provided the instrument has been suitably calibrated. The ALC method is preferred for reasons of convenience, but it also has the potential for much more precise measurement of the exhaust fractions than the 20% error found with the GC method.

C. Sensitivity to Fuel Composition

The UV response per unit of mass to exhaust fractions derived from different fuels was expected to vary with the composition of the fuel, since the absorbtivities of the various aromatic species cover a wide range. we have analyzed a number of fuels to determine their ALC response. These fuels included those used in the variables study (Section VIII) and others representing the range of fuels suitable for use in diesels which are commonly available. The results, along with certain characteristics of the fuels, are given in Table 13. The ALC response varies in a regular manner with fuel composition. The response is divided into two main categories due to the No. 1 and No. 2 fuel types. Fortunately there is a wide separation between these two main differences. The variation in response with aromatic composition is shown in Figure 13 (symbols code given in Table 13). The only grossly irregular point is the one for Soltrol 200 which is a special narrow cut--aromatics free fuel. By suitable calibration procedures, we believe it will be a simple matter to select the correct ALC sensitivity curve from an analysis of the fuel used in the exhaust study.

D. Response to Exhaust Odor Fractions

In examining the sensitivity of the ALC response to composition, the odor fractions isolated from the samples obtained in the variables study were also studied. These data are summarized in Table 14. The response for each of the LCA or LCO fractions derived from No. 1 fuel are the same, while the differences due to fuel composition are apparent in each. These sensitivity factors will have to be defined in detail to obtain appropriate calibration curves for each fraction.

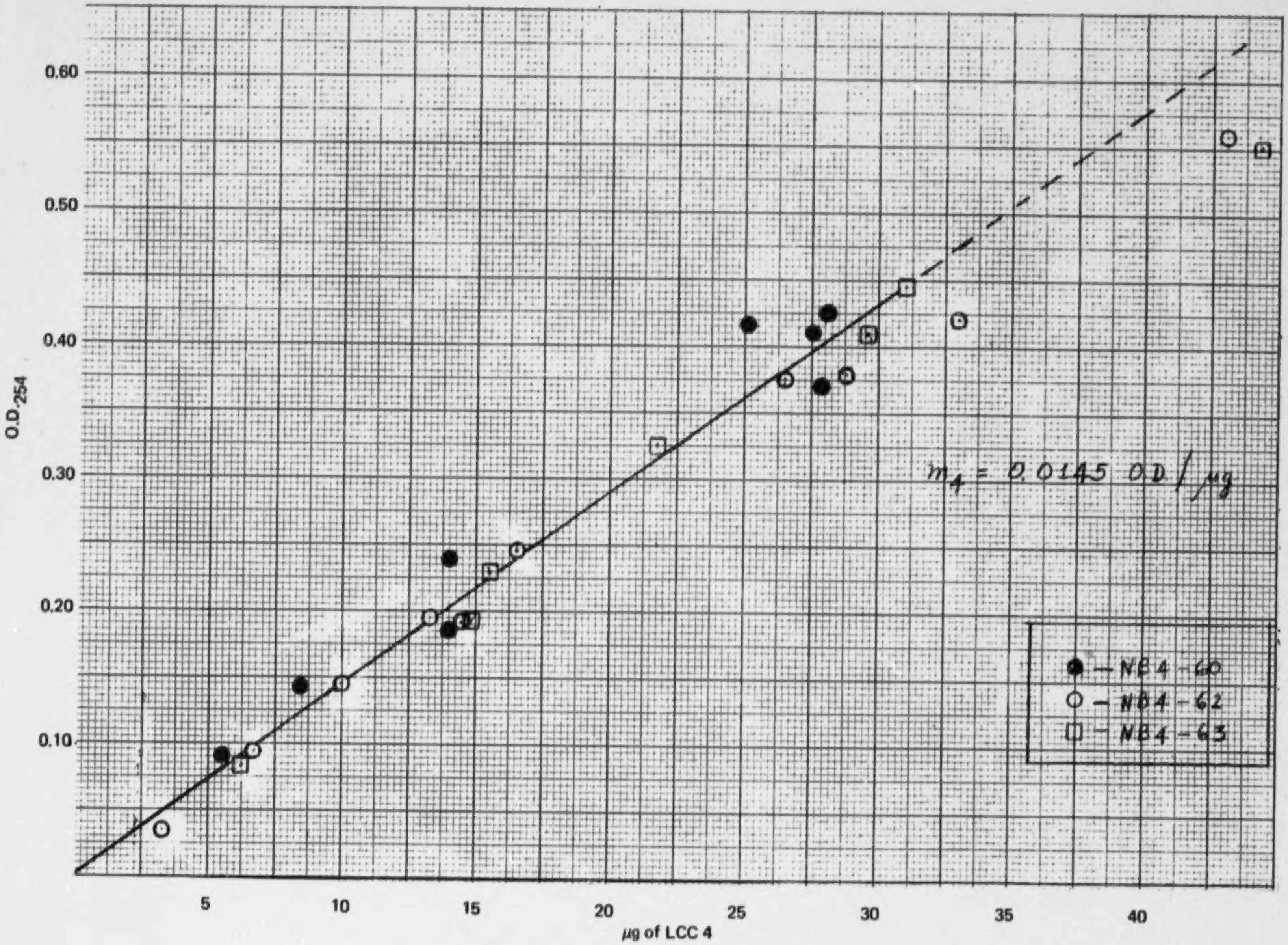

FIGURE 10 CALIBRATION CURVE FOR LCC 4 OF NO. 1 DIESEL FUEL

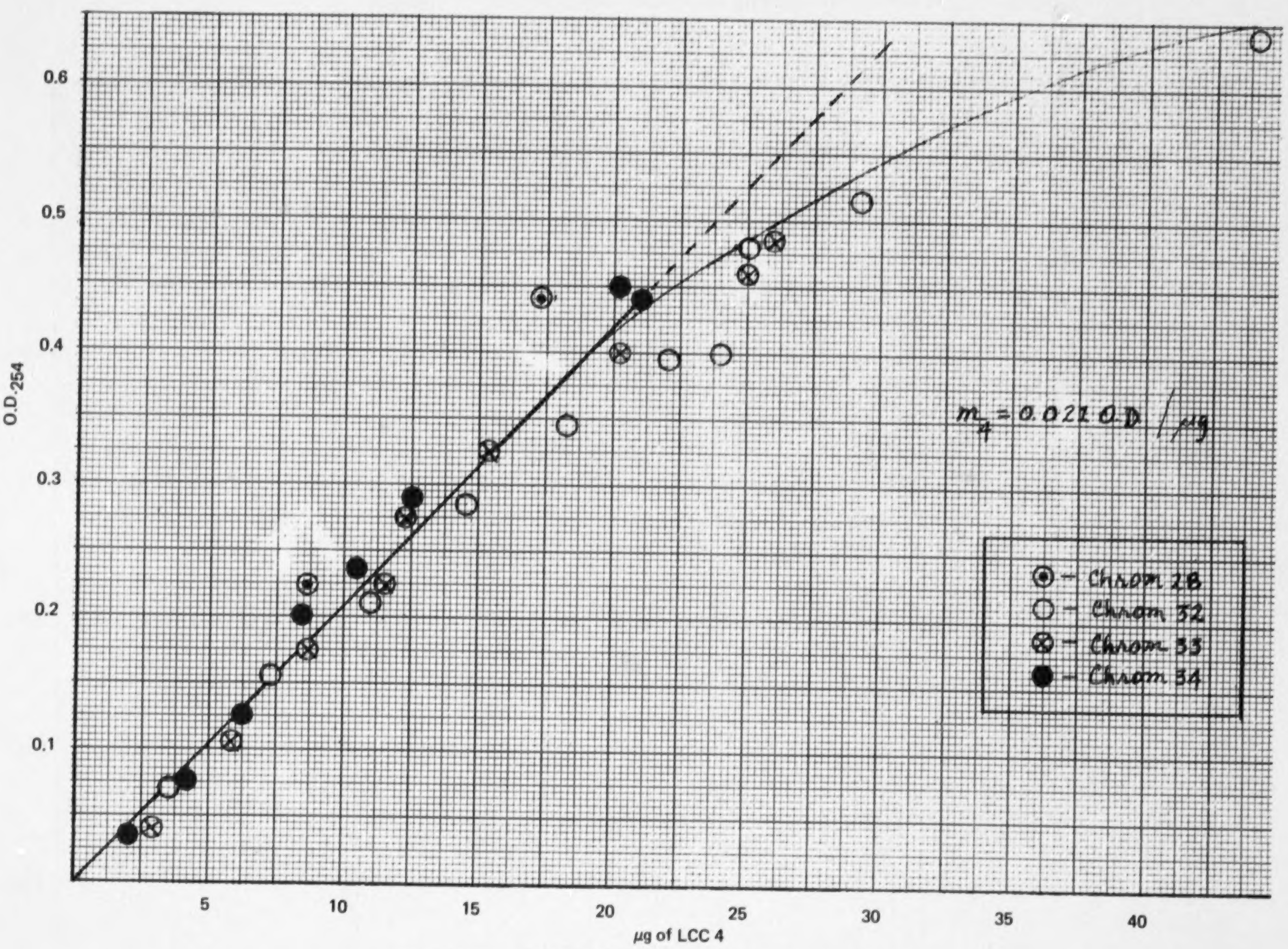

FIGURE 11 CALIBRATION CURVE FOR DIESEL EXHAUST LCC 4

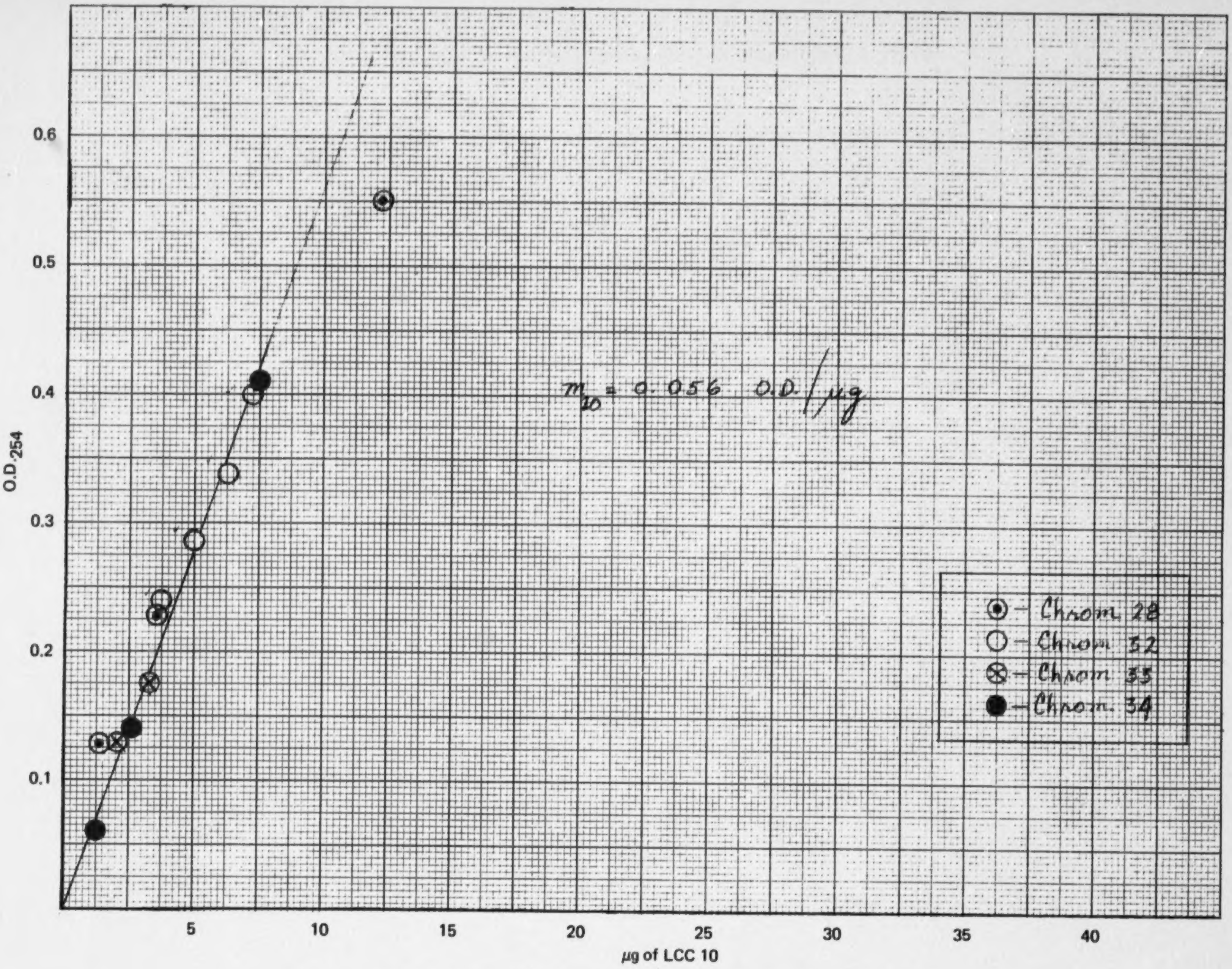

FIGURE 12 CALIBRATION CURVES FOR DIESEL EXHAUST LCC 10

Table 12

Comparison of ALC and GC Analysis Methods

Sample CHROM	Analysis Method	Peak No. 1 LCA	Peak No. 2	Peak No. 3 LCO
32	GC	38	1.2	4.5
	ALC	31	0.6	4.4
33	GC	38	-	6.4
	ALC	40	1.2	6.3
34	GC	40	1.9	5.0
	ALC	40	1.2	6.3

Table 13

Physical Characteristics and ALC Response of Various Fuels

	Fuel Type	Specific Gravity	%Aromatics	ALC Response OD/μg LCA: Based on Aromatics Composition		ALC Response OD/μg LCA: Based on GC Determined Mass of LCA	Distillation Point: 10%	Distillation Point: 50%	Distillation Point: 90%
X	Kerosene (61611)	0.812	16.5	0.0089	0.011	0.0088	375	405	459
X	Kerosene (60064)	0.808	16.0	0.0105			372	414	456
X	Kerosene (61338)	0.820	16.5	0.0108			379	421	477
○	Soltrol 200*	0.780[2]	1.3[2]	0.0115			460	478	495
△	No. 1 Diesel*	0.832	20.8	0.0120		0.0145	396	436	497
X	Kerosene (61835)	0.811	16.5	0.0135			379	415	462
O	No. 2 Diesel (East Coast)	0.826	24.1	0.030	0.044	0.041	424	482	566
O	No. 2 Diesel (61836)	0.849	32.0	0.034			414	486	554
O	No. 2 Diesel (Midwest)*	0.852	34.7	0.040		0.051	418	506	586
O	No. 2 Diesel (61339)	0.863	37.5	0.040			434	508	592
O	No. 2 Diesel (61610)	0.852	30.5	0.0456			430	504	586
O	No. 2 Diesel (60063)	0.837	28.0	0.054			404	472	562
☐	Heating Oil (East Coast)	0.854	35.4	0.064		0.085	430	498	585
☐	Heating Oil (Midwest)					0.064			

---

[1] - The mass was estimated on the basis of % aromatics composition.

[2] - These values are based on our analytical data.

* - Variables study fuels (Section VIII)

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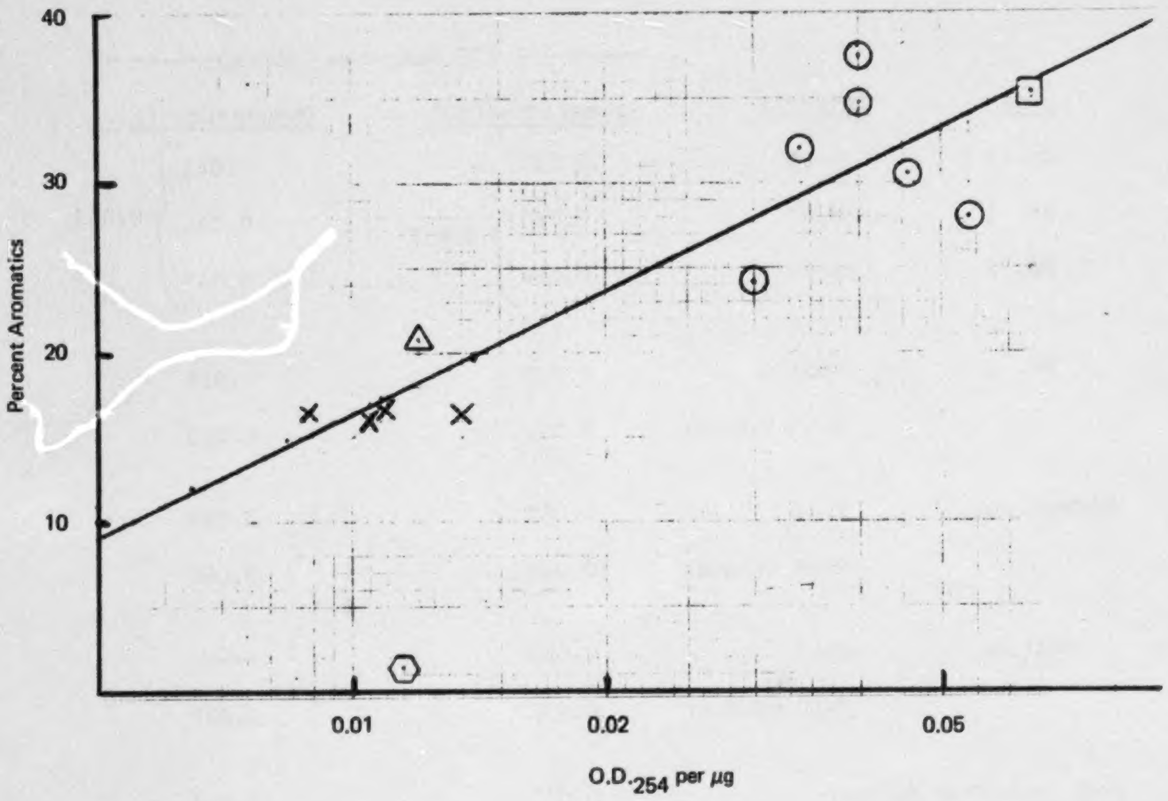


FIGURE 13 VARIATION OF ALC RESPONSE WITH AROMATIC CONTENT OF FUEL

Table 14

ALC Response Sensitivity to Exhaust Variables Studied

		ALC Response (OD/μg)			
Fuel	Injector	Aromatics (LCA)		Oxygenates (LCO)	
No. 1	S-60	0.013	0.017	0.041	0.043
No. 1	N-60	0.020		0.046	
No. 1	LSN-60	0.019		0.043	
No. 1	Fuel	0.051		0.038	
	N-60 exhaust	0.017		0.043	
Midwest No. 2	Fuel	0.051		0.069	
	N-60 exhaust	0.050		0.066	
Soltrol	Fuel	0.012		-----	
	N-60 exhaust	0.012		0.025	
Avg excluding Midwest		0.015		0.043	

VIII. STUDY OF ENGINE AND FUEL VARIABLES

Several test parameters including load, fuel, and injectors have been selected for study in order to examine the adequacy of our identification data. These variables were also chosen to provide the range of data for establishing the quantitative relationships between exhaust odor and chemical composition. Results on the effect of engine load have been previously reported (3). The exhaust odor intensities at 10%, 33%, and 90% load were all quite similar.

In these recent tests the old style S-60 injectors and the new low sac LSN-60 style were compared with the standard N-60 injectors which have been used in most of our studies. A high aromatics content Midwest No. 2 diesel fuel and a special aromatics-free paraffin fuel, Soltrol 200, were also studied to examine these variables. The pertinent characteristics of these fuels were summarized in Table 13.

Two to four sets of experiments were run for each of the variables studied. The average quantitative results of these studies are summarized in Tables 15 and 16 for the analytical and odor data. The 4-71 engine was run at 33% load and 1800 rpm for each of these studies. The dose/response odor data are also shown graphically in Figures 14-16 for the exhaust and LCA and LCO odor fractions. The detailed composition analysis of the odor fractions from each of these conditions is given in Table 17.

The S-60 injectors condition is the only one which gives clearly different exhaust results. The odor intensity of all of the other conditions is quite similar (Figure 14). Use of No. 2 fuel led to an exhaust odor character change with a substitution of terms such as the use of a tarry descriptor for the kerosene and smoky character notes. This may be consistent with the higher molecular weight aromatics such as acenaphthenes (Class 5 in the aromatics mass spec analysis) present in the fuel. Exhaust from the Soltrol 200 fuel has a completely different odor character than normal and is best described as smoky-candle and sour-oxidized.

Perhaps the most surprising part of these data, both from chemical analysis and sensory observation, is the closer similarity of results with the S-60 injectors to the data for the No. 2 fuel—instead of being similar to the No. 1 reference fuel. The exhaust odor character with the S-60 injectors was somewhat similar to that observed with Midwest No. 2 fuel in the heaviness of the odor notes as compared with the reference conditions.

The total hydrocarbon levels for the three injectors is consistent with the sac volumes (S-60 = 175 mm^3, N-60 = 3.5 mm^3, LSN-60 = 0.5 mm^3) as reported by Ford, Merrion, and Hames (6). The hydrocarbon emission level also drops with the No. 2 fuel again as noted by Ford *et al*.

The odor intensity of the LCO fractions is generally greater than that of the LCA fraction (Table 16) and is about the same as the exhaust odor intensity.

The relationships between the data gathered in these experiments will be explored in the next section.

Table 15

Diesel Exhaust Variables Analytical Data Summary

-------- Variable---------				LCA		LCO	
				----Aromatics----		---Oxygenates---	
Fuel	Injector	THC (ppm)	TOE mg/Kℓ	mg/Kℓ	% of TOE	mg/Kℓ	% of TOE
No. 1	S-60	3100	1220	210	18%	14	1%
No. 1	N-60	620	230	39	17%	7	3%
No. 1	LSN-60	300	86	16	18%	5	5%
No. 2 - Midwest	N-60	550	145	38	26%	6	4%
Soltrol 200	N-60	590	230	8	4%	6	3%

Table 16

Diesel Exhaust Variables Odor Summary

		Odor[a]					
				LCA		LCO	
Variable		Exhaust		Oily-Kerosene		Smoky-Burnt	
Fuel	Injector	b	m	b	m	b	m
No. 1	S-60	2.15	1.50	1.80	1.60	1.95	1.65
No. 1	N-60	1.45	1.72	1.50	1.66	1.60	1.57
No. 1	LSN-60	1.50	1.50	1.15	1.30	1.50	1.52
No. 2	N-60	1.60	2.00	1.70	1.65	1.65	1.65
Soltrol	N-60	1.50	1.36	0.65	0.87	1.00	1.84

[a] $TIA = b + m \log C$; C in ℓ/m^3
at 1 ℓ/m^3 (1000/1 dilution) $TIA = b$

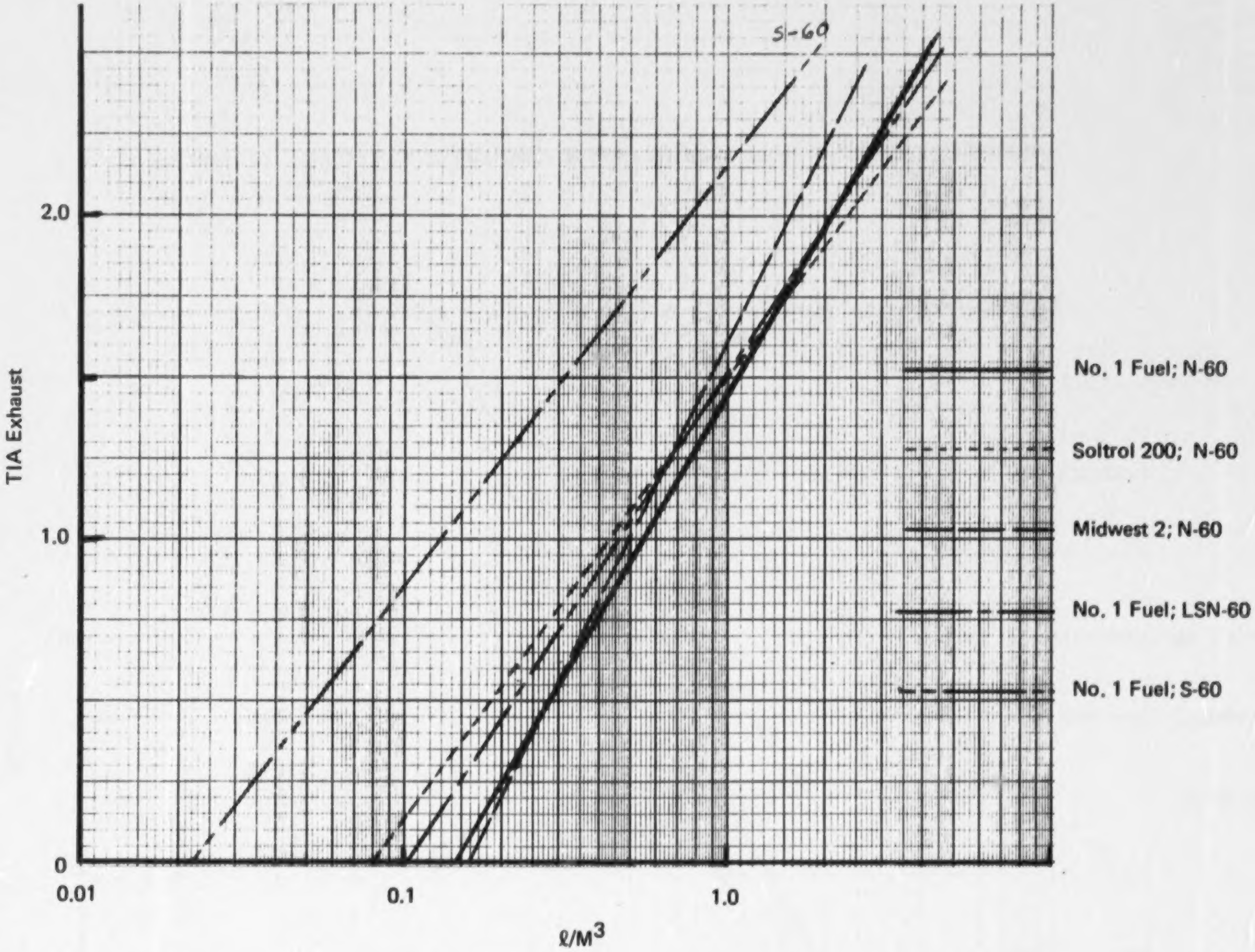


FIGURE 14 COMPARATIVE EFFECT OF FUEL TYPE AND INJECTOR DESIGN ON DIESEL EXHAUST ODOR (STATIC TEST ROOM)

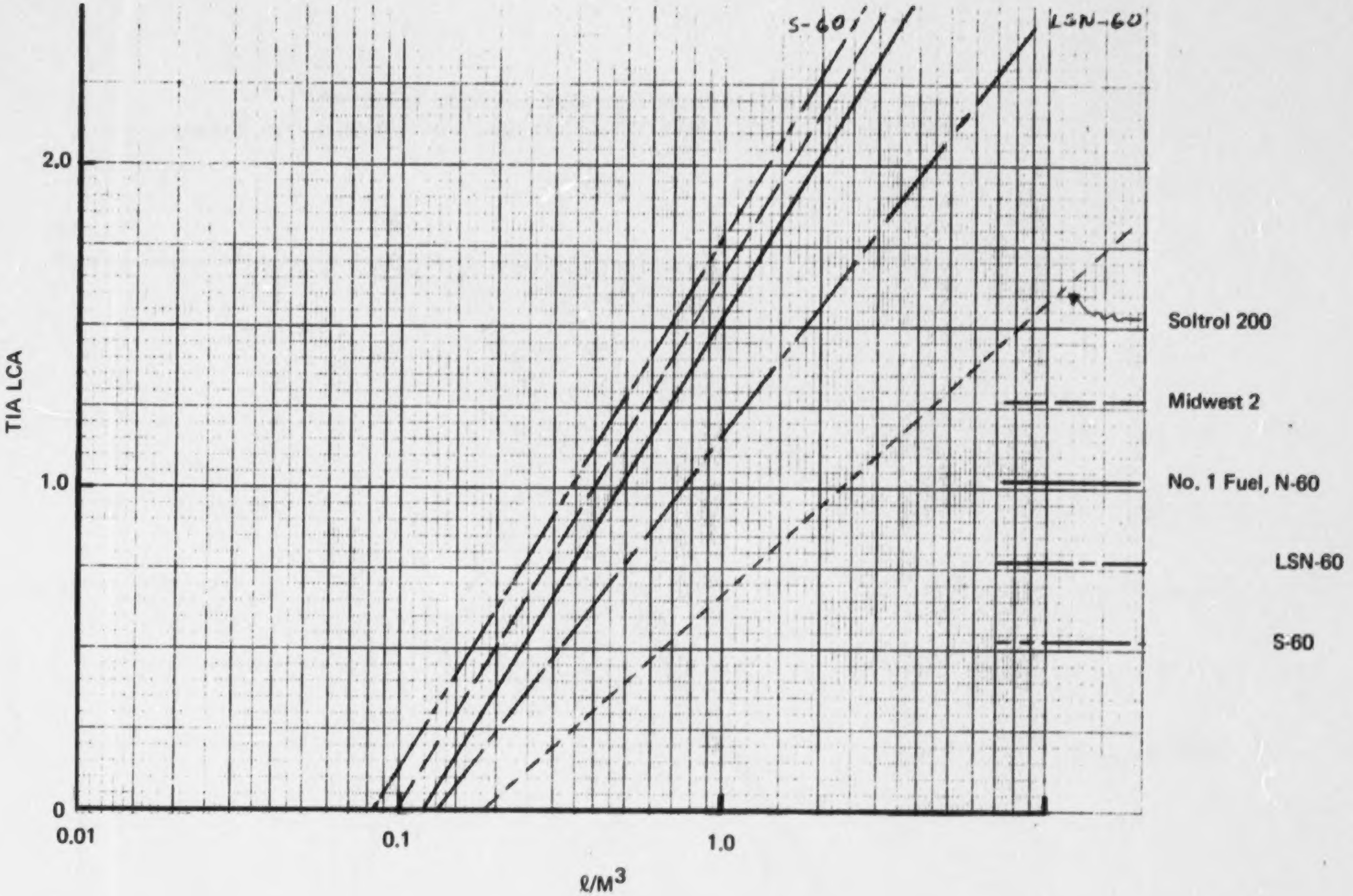


FIGURE 15 TIA OF LCA FRACTIONS: EFFECT OF FUEL TYPE AND INJECTOR DESIGN

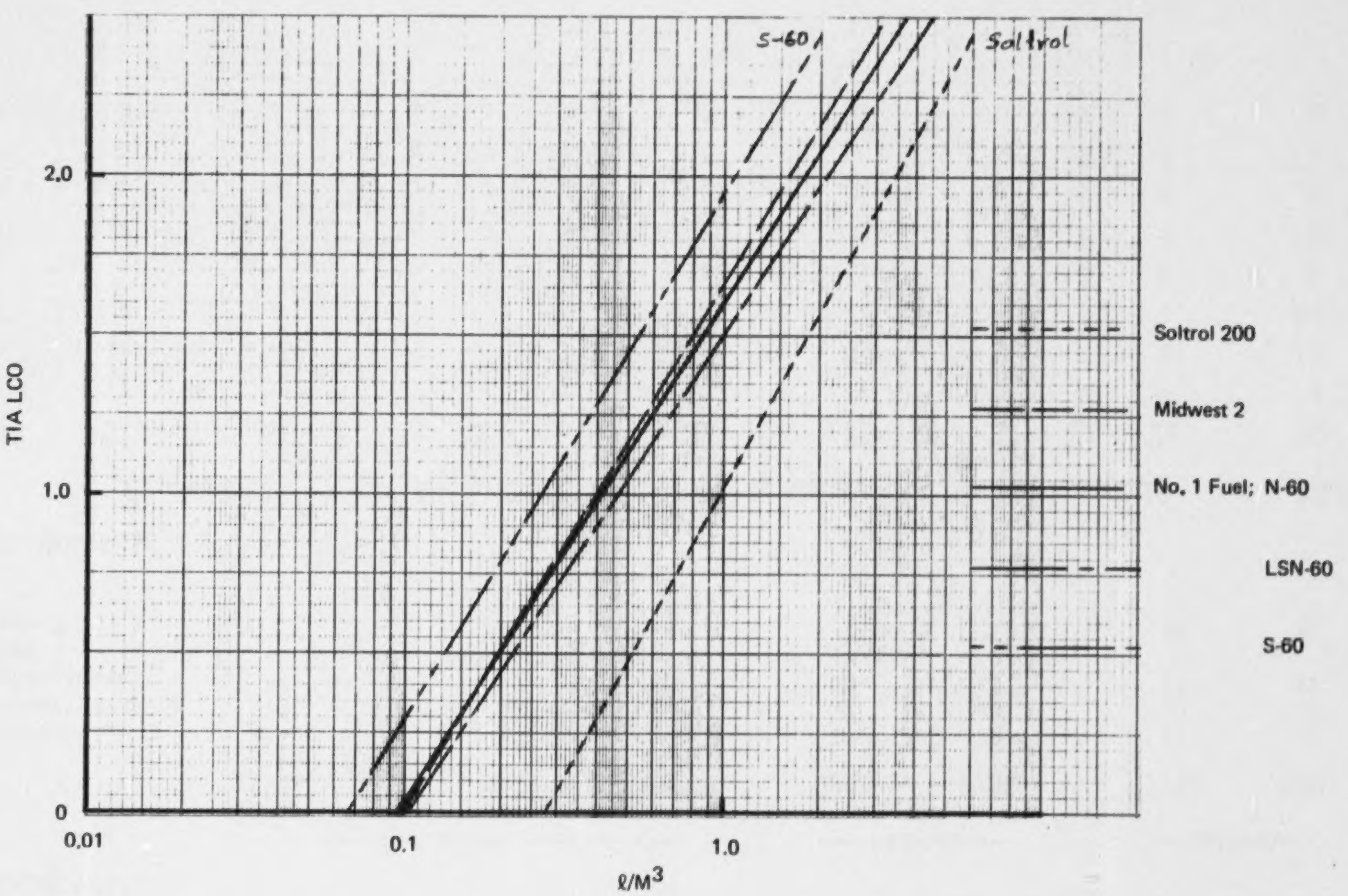


FIGURE 16 TIA OF LCO FRACTIONS: EFFECT OF FUEL TYPE AND INJECTOR DESIGN

Table 17

Mass Spectrometric Composition Analysis of Odor Fractions (%)

LCA, Aromatic

	No. 1 Fuel				Midwest		Soltrol	
	Fuel	S-60	N-60	LSN-60	Fuel	N-60	Fuel	N-60
Alkylbenzenes	54	61	62	50	17	30	19	23
Indans/Tetralins	28	24	23	28	22	23	43	28
Naphthalenes	20	16	17	21	52	43	14	12
Class 4					8	3	-	
Class 5					2	1	24	37

LCO, Oxygenate

	No. 1, S-60			No. 1, N-60			No. 1, LSN-60			Midwest, N-60			Soltrol, N-60		
R+DB	O_1	O_2	O_3	O_1	O_2	O_3	O_1	O_2	O_3	O_1	O_2	O_3	O_1	O_2	O_3
1	1	0	0	1	0	0	2	0	0	1	0	0	3	1	0
2	11	2	0	15	1	0	12	6	0	12	1	0	18	4	0
3	9	3	0	13	2	0	15	4	0	8	2	0	17	8	0
4	7	3	0	10	2	0	12	3	0	8	2	0	11	5	1
5	10	4	0	16	3	0	8	4	0	14	6	0	5	4	1
6	21	4	1	13	3	1	13	4	0	10	6	0	8	3	0
7	8	2	1	4	2	0	6	2	1	9	3	0	3	1	0
8	8	1	1	5	1	0	7	1	0	10	2	0	2	1	0

IX. CORRELATION OF ANALYTICAL AND ODOR DATA

A. Odor Interaction of Kerosene and Smoky-Burnt Fractions

In attempting to correlate observed engine emissions with odor intensity, it was necessary to determine the odor interaction between the two isolated odor fractions, LCA and LCO. If either one alone best represented the exhaust odor intensity, then it would be sufficient to measure all or some part of that group to determine the exhaust odor. If, on the other hand, there were a synergistic effect between the groups, then it would be necessary to measure both groups in some combined manner.

This matter was studied by measuring the odor intensity of the total organic extract (TOE) and the LCA and LCO fractions and then combining ¼ of each LCA and LCO fraction with the whole of the other. The odor results obtained from the study in the dynamic test chamber are given in Table 18 and are depicted graphically in Figure 17.

It appears from these data that there are no unusual effects of one odor fraction on the other. Also, the exhaust odor intensity (TOE) is accurately represented by the odor of the LCO fraction.

This matter was explored further by comparing the odor intensities of the exhaust and the LCO odor fractions. A comparison of the odor intensities calculated at 1 ℓ/m^3 from the dose/response data for these two samples (exhaust and LCO) in the variables study is shown in Figure 18. These data clearly show the accuracy with which the exhaust odor may be represented by the LCO smoky-burnt odor fraction for normal exhaust conditions. The only poor correlation is for the exhaust from the unusual Soltrol fuel.

B. Correlation of Odor Intensity and Sample Mass

The ultimate test of the approach we have developed comes in examining how well the quantity of the two primary odor fractions represents the odor of those fractions and the exhaust. The data from the variables study is summarized in Table 19. We have represented the odor intensity of the exhaust and its fractions by the value computed for the 1000/1 dilution (1 ℓ/m^3). This concentration is in the centroid of our data and represents a realistic roadway dilution.

The correlation of LCA odor intensity and abundance is shown in Figure 19. The data correlate over this limited range within the precision of the odor data with the exception of the Soltrol Fuel. A similar plot for the LCO fraction is shown in Figure 20 with comparable results. The final test of these approaches comes in the correlation of the exhaust odor intensity with abundance of the LCO fraction as shown in Figure 21. The correlation is promising, but premature, considering the small amount of data available for evaluation.

These approaches appear to offer a means of predicting exhaust odor intensity based on the simple measurement of the primary odor fraction abundance using the ALC procedure. Further data will be required representing a wider range of emissions to fully test this approach.

It should be remembered that the success of this simplified approach has been based on a detailed understanding of the odorous chemical species present in each fraction and their relationship to total exhaust odor.

Table 18

Odor of Mixtures of LCA and LCO (TIA)[a]

Dose (ℓ/M^3)	TOE	LCA	LCA + LCO/4	LCA + LCO	LCA/4 + LCO	LCO
0.2	½	¼	½	3/4	½	¼
0.4	2	½	½	1	1	1½
0.8	2	1	1	1 3/4	1 3/4	2
0.8	1½	1	1½	1½	2	1 3/4
1.6	2½	1½	1½	2	2	2¼
3.2	2 3/4	2	2	2½	2½	2½
1.0[b]	1.9	1.2	1.3	1.7	1.8	1.8

(a) Sample Chrom 35

(b) Calculated from least squares data, TIA = b + m log C

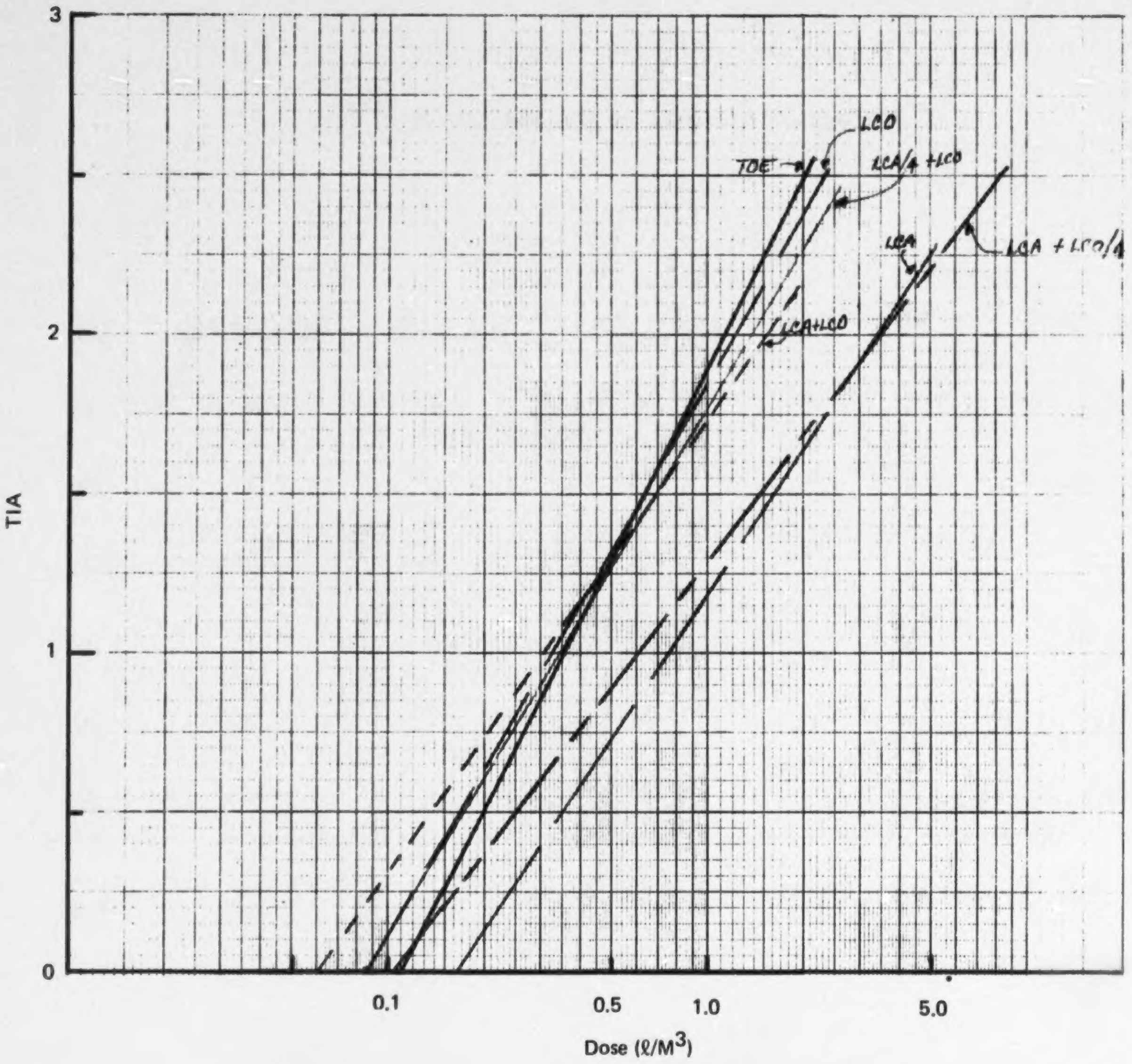


FIGURE 17 STUDY OF LCA-LCO INTERACTION EFFECTS

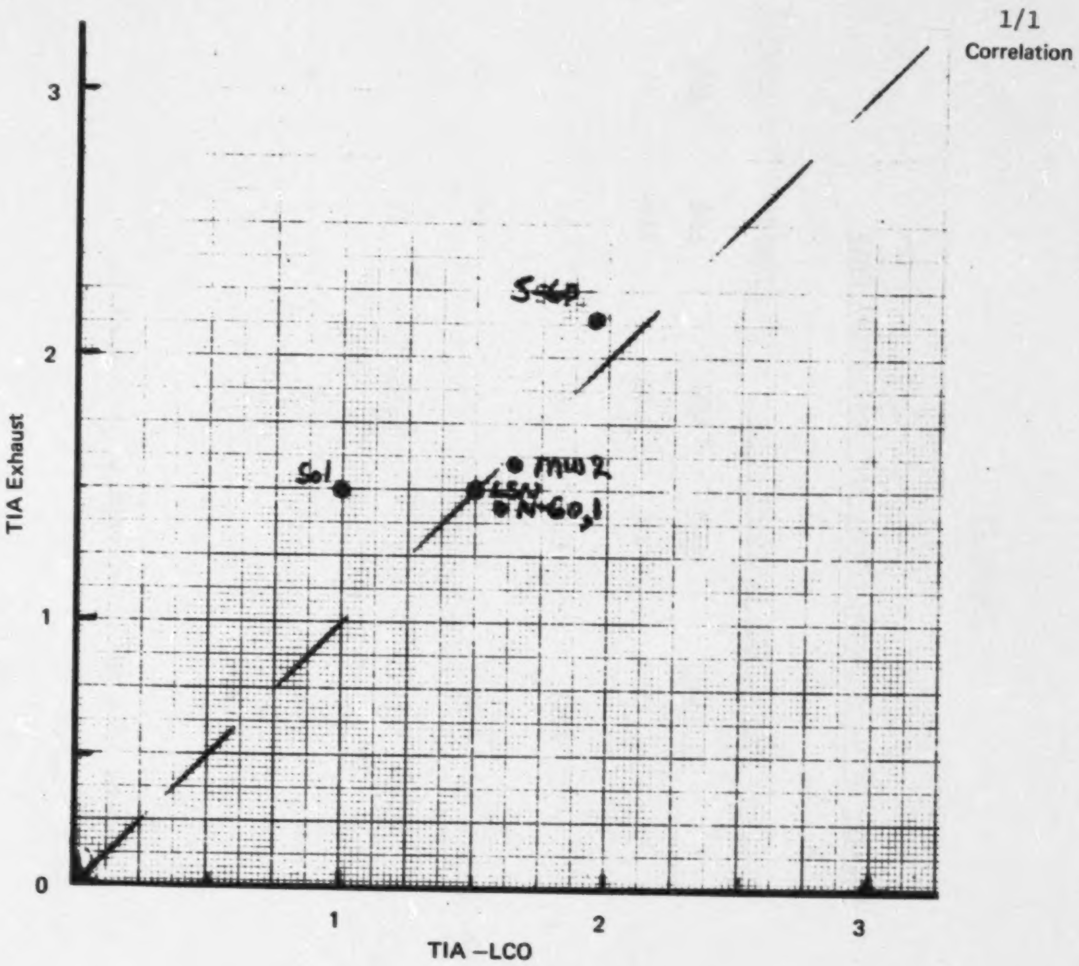


FIGURE 18 COMPARISON OF EXHAUST AND LCO ODOR INTENSITIES

Table 19

Summary of Correlatable Odor and Analytical Data

	TIA (1 ℓ/M³)[a]			Concentration (μg/ℓ)[b]	
	Exhaust	LCA	LCO	LCA	LCO
S-60, No. 1	2.15	1.8	1.95	210	14
N-60, No. 1	1.45	1.5	1.6	39	7
LSN-60, No. 1	1.5	1.15	1.5	16	5
Midwest No. 2	1.6	1.7	1.65	38	6
Soltrol	1.5	0.65	1.0	8	6

a. Computed from the dose/response observations.

b. μg/ℓ ≡ mg/kℓ

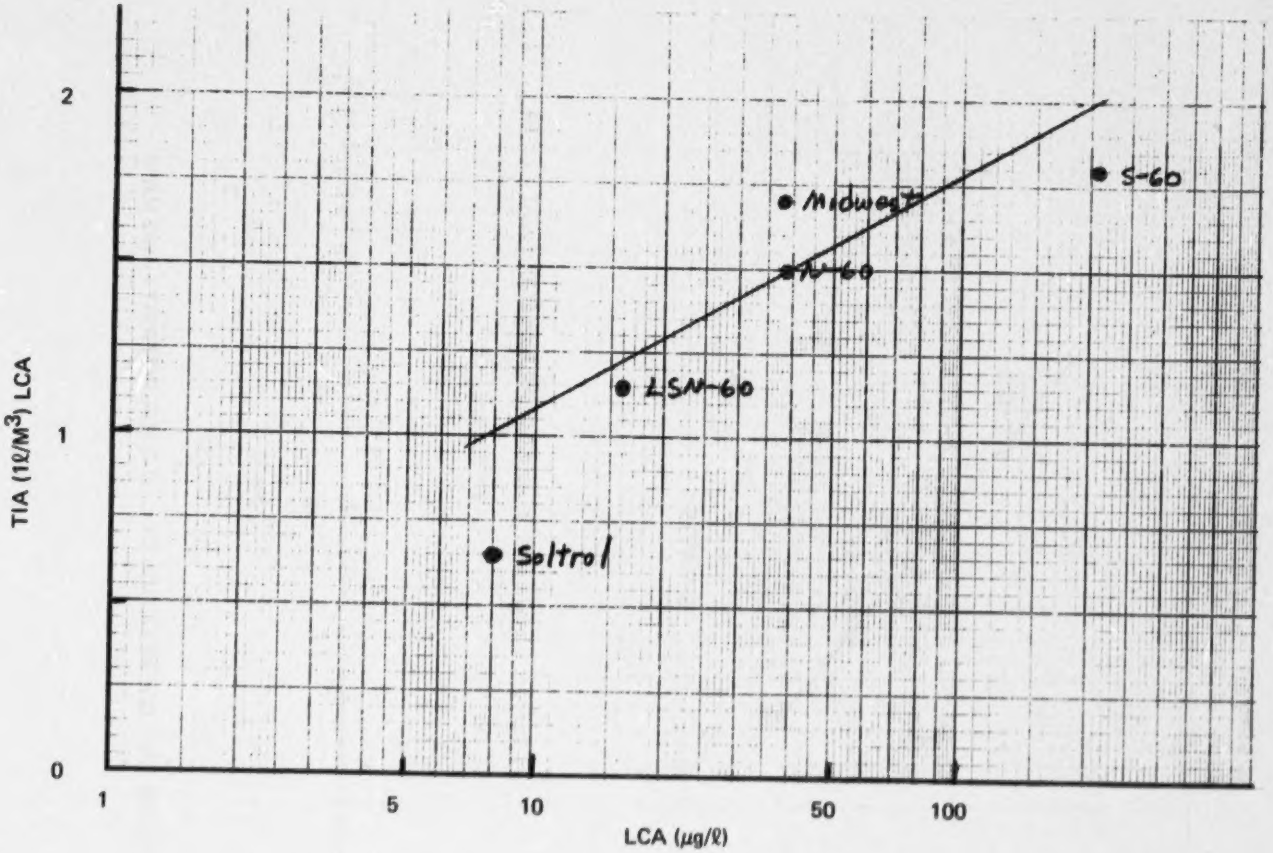


FIGURE 19 CORRELATION OF LCA ODOR INTENSITY AND MASS

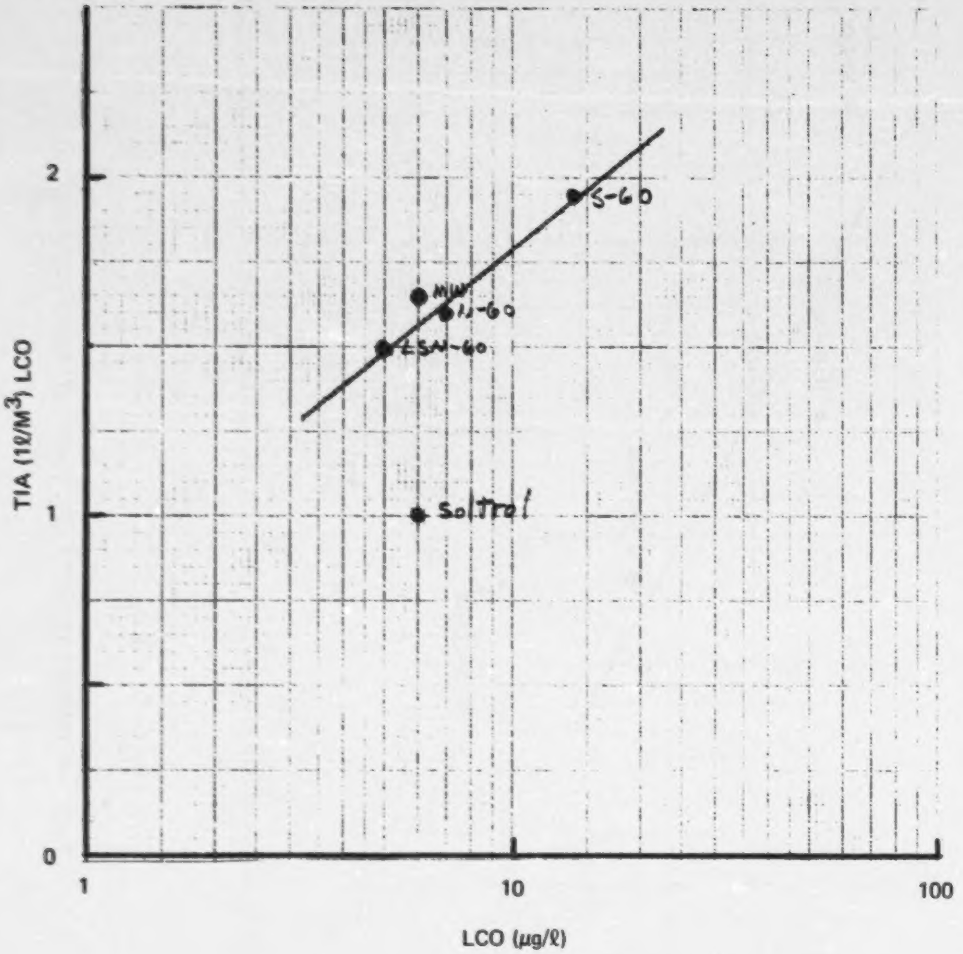


FIGURE 20 CORRELATION OF LCO ODOR INTENSITY AND MASS

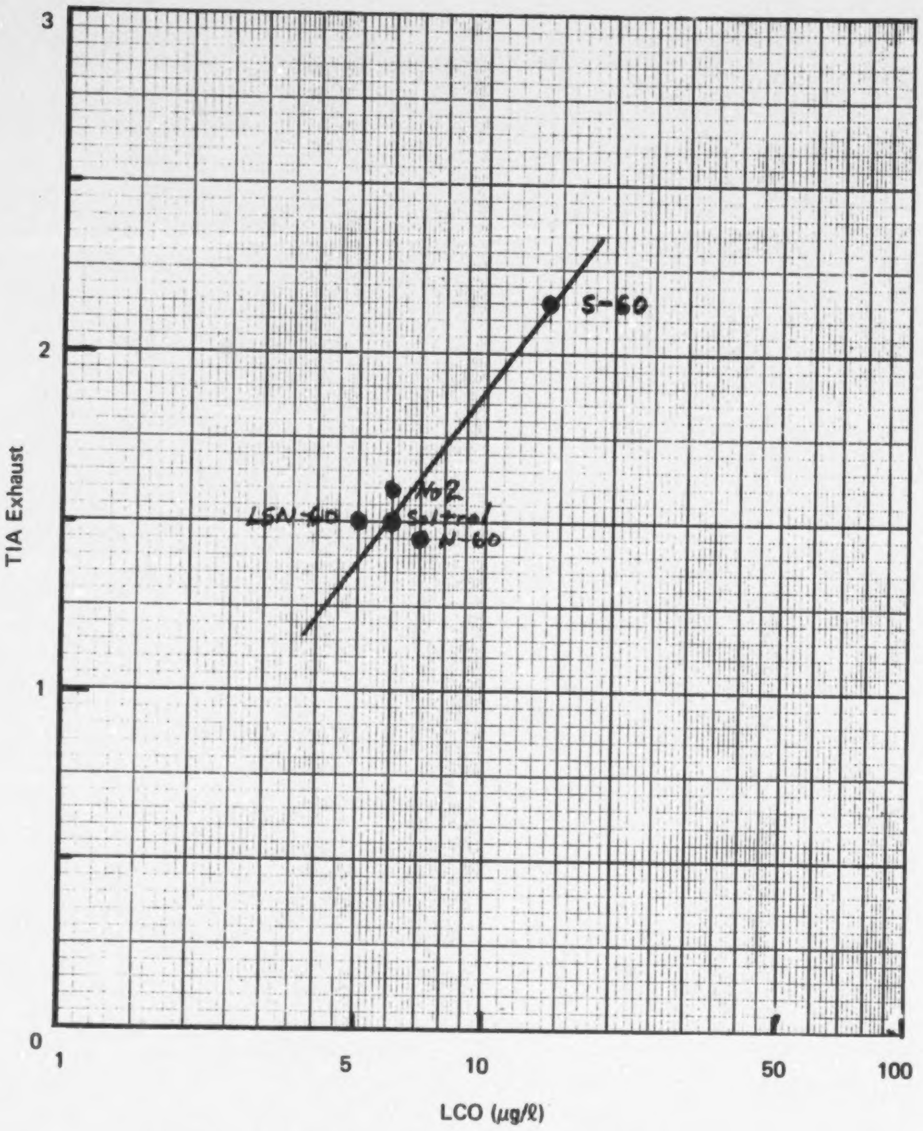


FIGURE 21 CORRELATION OF EXHAUST ODOR INTENSITY WITH LCO

X. REFERENCES

1. Chemical Identification of the Odor Components in Diesel Engine Exhaust, final report July 1969, CRC Project CAPE-7-68, HEW Contract PH 22-68-20.

2. Chemical Identification of the Odor Components in Diesel Engine Exhaust, final report June 1970, CRC Project CAPE-7-68, HEW Contract No. CPA 22-69-63.

3. Chemical Identification of the Odor Components in Diesel Engine Exhaust, final report June 1971, CRC Project CAPE 7-68, EPA Contract No. EHSD 71-18.

4. F. W. McLafferty, "Interpretation of Mass Spectra," Benjamin New York, 1966.

5. Chemical Species in Engine Exhaust and their Contributions to Exhaust Odors, Report No. IITRI C6183-5, final report November, 1970.

6. H. S. Ford, D. F. Merrion, and R. J. Hames, "Reducing Hydrocarbons and Odor in Diesel Exhaust by Fuel Injector Design", SAE Paper 700734 presented in Milwaukee, Wisconsin, September, 1970.

APPENDIX A

EXPERIMENTAL TEST FACILITY

The test facility used for these studies is shown schematically in Figure A-1 and consists of engine, odor, and sample areas. The engine used is a 71 series 4-cylinder diesel[*]. Operating at a constant speed of 1800 rpm, most of the work has been done at 33% load using No. 1 diesel fuel. The three component resistance load (10 KW and two 30 KW) allows us to operate at 10-90% load.

The static odor chamber is described in detail in Appendix B. Sample collection for analysis had initially been done using various condenser systems, and these are still required when sufficient sample (10,000 - 100,000 liters) is needed to run a complete analytical identification series. However, now that the composition is known, we find that all of the required analyses can be achieved on the material isolated from 500 - 1000 liters of exhaust. The sorbent tube collection method described in Appendix D is preferred for these purposes.

[*] Detroit Diesel Allison Division of General Motors Corporation Model 4154N

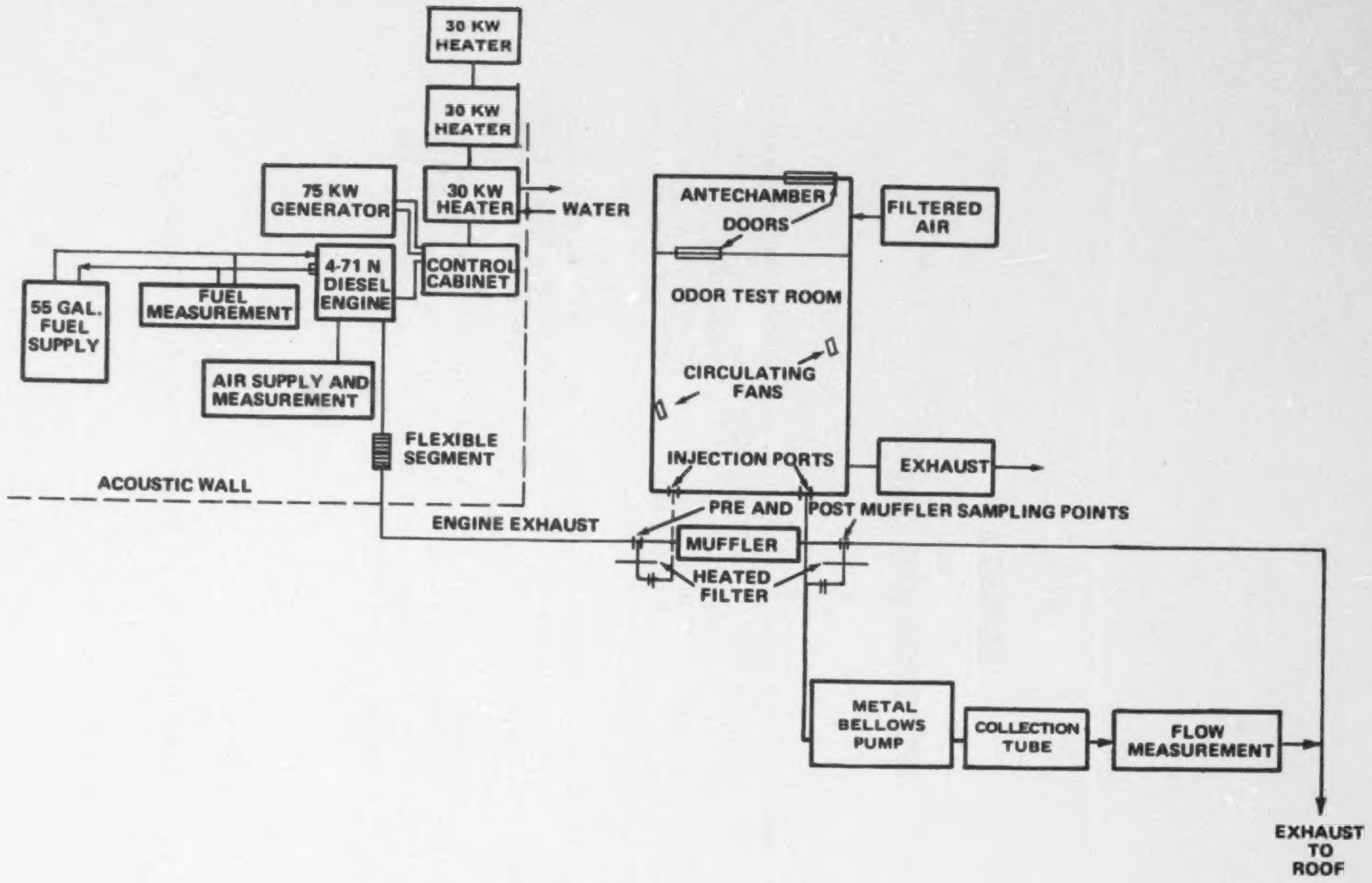

30 KW HEATER
30 KW HEATER
75 KW GENERATOR
30 KW HEATER
WATER
4-71 N DIESEL ENGINE
CONTROL CABINET
55 GAL. FUEL SUPPLY
FUEL MEASUREMENT
AIR SUPPLY AND MEASUREMENT
FLEXIBLE SEGMENT
ACOUSTIC WALL
ENGINE EXHAUST
ANTECHAMBER
DOORS
FILTERED AIR
ODOR TEST ROOM
CIRCULATING FANS
INJECTION PORTS
EXHAUST
PRE AND POST MUFFLER SAMPLING POINTS
MUFFLER
HEATED FILTER
METAL BELLOWS PUMP
COLLECTION TUBE
FLOW MEASUREMENT
EXHAUST TO ROOF

FIGURE A1 EXPERIMENTAL ARRANGEMENT OF DIESEL ENGINE, ODOR TEST ROOM, EXHAUST SAMPLING AND COLLECTION SYSTEM

APPENDIX B

ODOR PROFILE MEASUREMENTS*

1. DIESEL EXHAUST ODOR

The standard diesel exhaust sample has normally been obtained from a 4-71 diesel engine operating at 33% load and 1800 rpm on No. 1 diesel fuel. The profile analysis of the standard sample diesel exhaust was consistent from day to day, but the odor of diesel exhaust did show some differences with variations in engine operation. Preliminary studies indicate that within the normal procedural time interval between sampling and examination, there are no detectable losses. Indeed, the odor appears to persist with only slight change for over one hour. Total profile characterization is consistent with the odor observed when traveling behind a bus, which confirms our belief that the mode of engine operation provided a representative sample for analytical studies.

The description of the diesel exhaust odor in the static test room with a dilution ratio of 600:1 can be described by three character notes; oily, represented by technical grade hexadecane among other standards; burnt, which, although similar to a low dilution of propionaldehyde, phenol, and cresol, is produced in fuels with partial oxidation at elevated temperatures, and kerosene, which is the top odorous component of the fuel and may be described as having sweet, sharp, sour, tarry, and solvent components. In addition to these odor characteristics which appeared in the slight-to-moderate intensity range at this dilution, two feeling sensations - nose irritation and eye irritation - were apparent.

As implied by the descriptive terminology used, some of the odor characteristics are present in the fuel itself. The odor characterization of a 150-$\mu\ell$ aliquot of fuel, which (by computation) is equivalent to the amount of fuel burnt to produce the 21-liter sample of exhaust, produces an odor in the test room at least as strong as the exhaust odor. The dominant odor characteristic is kerosene, with the oily note being less intense and the burnt aroma barely detectable. With the diesel exhaust, the oily and burnt aromas are primary character notes and kerosene a supplementary factor.

---

* Taken in part from Final report of third year's work, June 1971, "Chemical Identification of the Odor Components in Diesel Engine Exhaust."

2. ODOR PROFILE METHODOLOGY

The Odor Profile Method of analysis has proven useful in flavor and odor studies in a wide range of food and nonfood products. The Profile Method, which originated at Arthur D. Little, Inc., 25 years ago, is a semiquantitative and qualitative description of the odor sensation. The total odor sensation can be described by six character notes. The method is qualitative in that there is verbal description as to the odor quality(s) perceived. The order of appearance of odor character notes indicates the other odor qualities present as a function of time on a microsecond basis.

The intensity of each character note (as well as the Total Intensity of Aroma, TIA) is rated on a four-point scale ranging from threshold-)(, slight-1, moderate-2, to strong-3 intensities. It has been our experience that for the odor intensity to increase by one unit (i.e., from slight to moderate), a ten-fold increase in concentration is required. The threshold intensity indicates that the character note detected is just recognizable. The basic four point scale of threshold-)(to strong-3 intensity can be expanded into a seven point scale with experienced panelists by the use of one-half ratings. Thus, the full scale of intensity rating of the odor strength is summarized below:

Numerical Rating	Intensity
)(	Threshold (recognition)
½	Very slight
1	Slight
1½	slight to moderate
2	Moderate
2½	Moderate to strong
3	Strong

The presence of feeling sensations is indicated by a check mark (✓) without any effort to describe their intensity. Four trained analysts form the odor profile panel. The sample to be analyzed is presented to the panelists in a standard manner. In this study, each of the four panelists entered the odorized test chamber independently of one another and sniffed the air three times. Each then recorded his observations on the odor character notes perceived, their order of appearance, and their intensity. After the observations in the test room, the panelists gathered to discuss their results. Reference was made to odor standards to relate the various verbal descriptions used and to develop common language in describing the odor quality. Reference odor standards may be single chemical species or may refer to a mixture of chemicals.

The panel's results were then composited into an odor profile that summarized the odor observations of the four panelists and indicated the odor quality, the order of appearance of the characteristic notes and their intensities.

3. STATIC ODOR TEST ROOM

The static odor test room consisted of an antechamber, an odor chamber, and supporting equipment such as fans, ducts, activated carbon, air intake, and air exhaust motors. The air is treated with activated carbon (C-42 cannister from Dorex) and provided a low-odor background diluting medium and was also used to flush odorized air from the chamber and acclimate the four panel members to a low odor background. The odor chamber where the odor studies were carried out was an aluminum-clad room with a volume of 12,600 ℓ. Previous studies have shown polished aluminum to be satisfactory for odor studies because it has a low odor background. Fans in both the odor chamber and antechamber ensured adequate mixing and assisted in flushing the test room with odor-free air.

The sequence of events occurring prior to an odor observation by the panel in the test room is listed below.

a. Odor-free air is used to flush out the antechamber and odor chamber.

b. The door connecting the odor chamber and antechamber is closed, thus sealing the odor chamber.

c. Diesel exhaust is injected into the odor chamber through a sampling line by means of a swivel-jointed sampling system. Most of the initial odor studies were done using a 600/1 dilution of exhaust obtained from a 21-liter sample. Three fans located in the odor chamber circulate the diesel exhaust with the diluting air to ensure proper mixing. Five minutes after injection the fans are shut down, and the odorized air in the odor chamber is allowed to come to rest.

d. The four panel members then enter the antechamber where they become acclimated to the low odor background air.

e. The panel then enters the odor chamber to make observations.

f. The cycle is then repeated to prepare the odor test room for the next observation. A 20-minute flushing period has been found to be adequate for removing odor from the test room.

4. DYNAMIC ODOR TEST CHAMBER

A dynamic odor test chamber has been constructed at ADL in conjunction with other research progrms being conducted on the basic characteristics of odor. This facility, shown schematically in Figure B-1, provides an excellent means for efficiently conducting the dose/response odor studies required for more precise determination of the odor intensity of exhaust samples.

The facility has been constructed based on the same general guidelines used for the static ahmber. It consists of a carbon filter to provide normally a 100 ℓ/sec odor-free air flow which is controlled by the exhaust fan. A remote controlled syringe drive introduces TOE, LCA, or LCO exhaust samples which are then thoroughly mixed in an ADL static mixer to insure homogeneous sample presentation in a laminar flow through the test chamber. The chamber (approximately 6 x 6 x 4') comfortably seats a single observer. Communication for reporting odor intensity and character is achieved through a microphone/headset combination.

During a test the odor analyst is not informed as to the time or order in which samples are presented. The analyst is instructed to report observations when perceived. A typical procedure would be as follows:

1. Analyst enters chamber, adjusts microphone, and adapts to odor-free background for three minutes.

2. A sample is injected for a period of 30 sec. at a predetermined concentration. Odor observations when perceived are reported verbally where they are recorded by the technician operating the facility from an adjacent room.

3. An odor-free background is presented for two minutes.

4. Sample presentation is conducted at a new concentration.

5. The sequence is repeated for the number of points required.

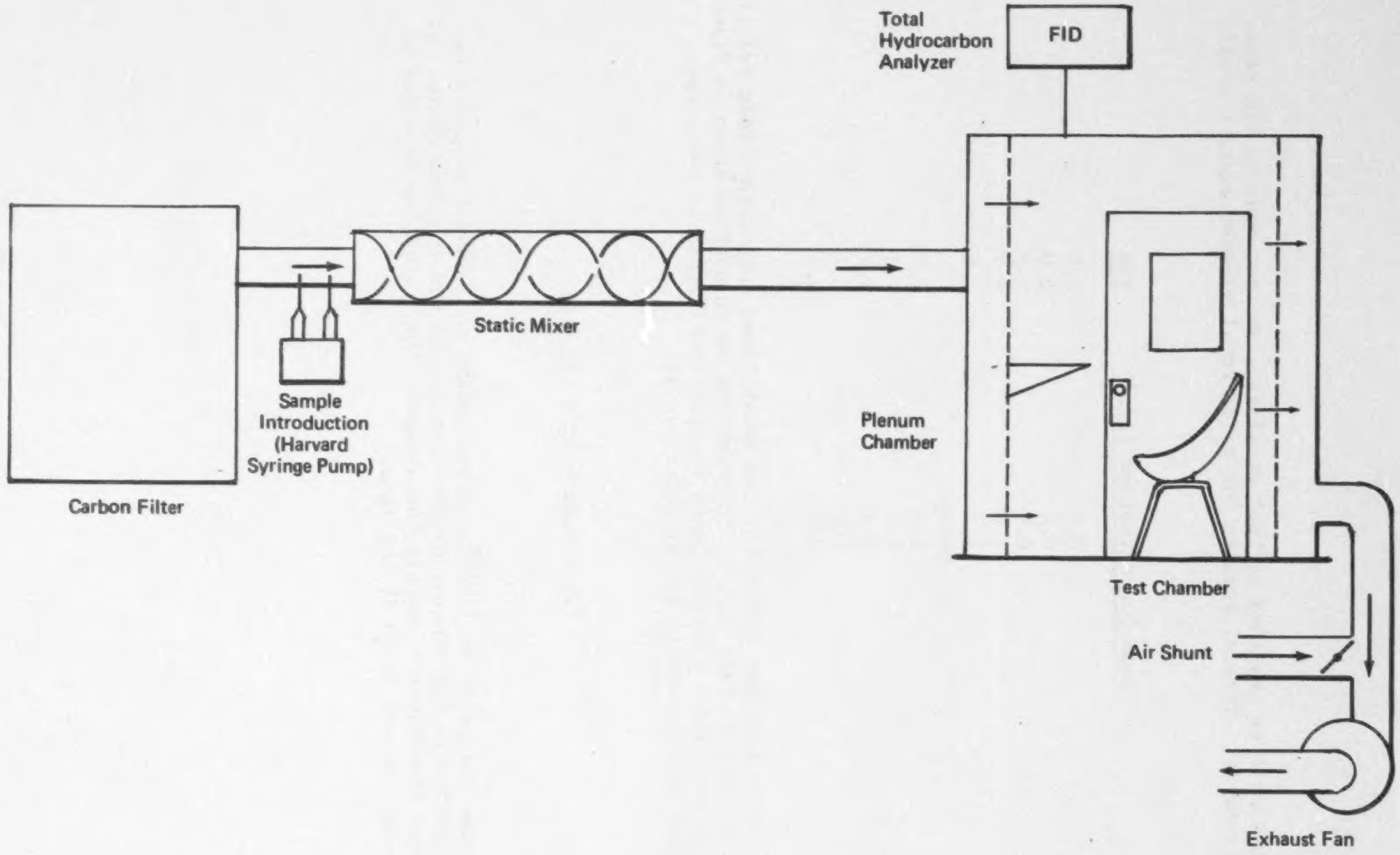

Total
Hydrocarbon
Analyzer
FID
Carbon Filter
Sample
Introduction
(Harvard
Syringe Pump)
Static Mixer
Plenum
Chamber
Test Chamber
Air Shunt
Exhaust Fan

FIGURE B-1 DYNAMIC ODOR TEST CHAMBER

Each sample is examined by four panelists, and the average TIA value is reported. Typical results for a TOE total exhaust extract would be:

Dose Concentration (ℓ/m^3)	TIA
0.2	0.5
0.4	1.0
0.8	1.5
1.6	1.75
3.2	2.5
break	
0.8	1.25
0.2	0.5
3.2	2.25
1.6	1.75
0.4	0.75

When these data are treated by the established semi-logarithmic relationship of sensory response, a dose/response curve such as shown in Figure B-2 is obtained. From the least squares correlation of these data, the exhaust odor intensity can be described as

$$\text{TIA} = 1.50 + 1.50 \log \text{Conc.}$$

The odor intensity at 1 ℓ/m^3, corresponding to a 1000/1 dilution is mathematically represented by the constant in the equation above. It is thus convenient to report the observed odor intensity in terms of the constant and slope of the line.

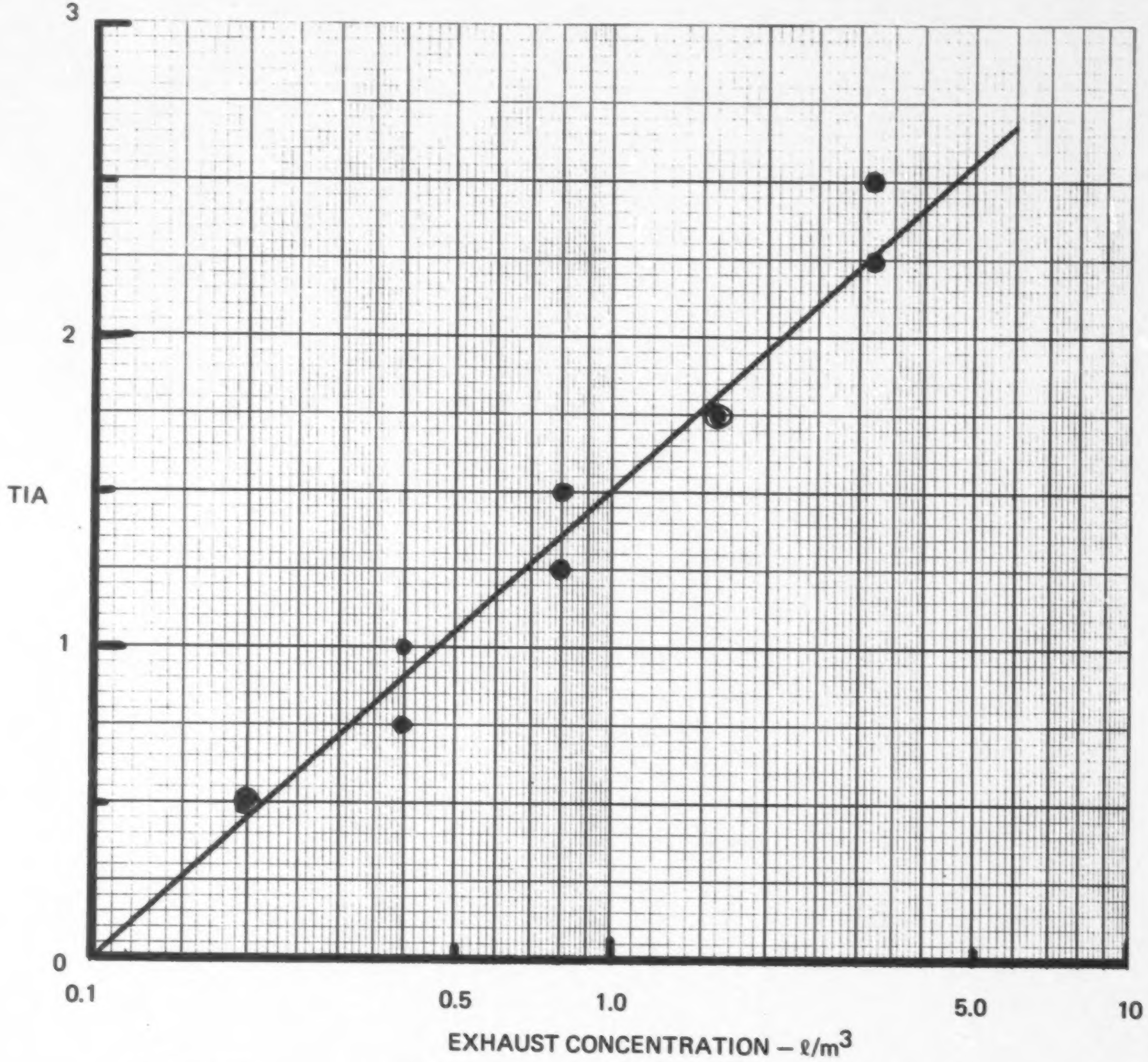


Figure B-2 DOSE/RESPONSE DETERMINATION OF DIESEL EXHAUST ODOR

APPENDIX C

CHEMICAL COMPOSITION OF THE ODOR COMPONENTS IN DIESEL EXHAUST

A detailed chemical description of the odorous compounds responsible for the characteristic diesel exhaust odor is given in the second and third year final reports of the CAPE-7-68 project (refs. 2 and 3). The conclusions of these studies are presented here for review purposes. In the sensory evaluation of diesel exhaust odor, we have described the odor as having two primary odor character groups, oily-kerosene and smoky-burnt, each contributing about equally to the exhaust odor intensity. The composition of each of these groups is summarized below.

1. Oily-kerosene

The oily-kerosene odor charcter group is isolated from diesel exhaust samples in the aromatic (LCA) fraction using the liquid chromatographic separation procedure described in Appendix E. The primary chemical species identified in this fraction are summarized in Table C-1. Using a No. 1 diesel fuel, the quantitative composition of this fraction was found to be typically

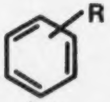
Species	Weight %
Alkyl benzenes	24
Indans/tetralins/indenes	14
Naphthalenes	57

Completion of the two-stage gas chromatography-odor-high resolution mass spectrometry analysis of this fraction revealed that the main odor contributor responsible for the kerosene type odor was the series of alkyl indans and tetralins. The alkyl benzenes were found to contribute to the oily odor character assisted by the indenes. No specific odor correlation was found with the naphthalenes, although they may contribute to the overall odor perception through some form of synergism.

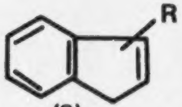
Table C-1

ODOR-STRUCTURE CORRELATION FOR THE OILY-KEROSENE ODOR COMPLEX

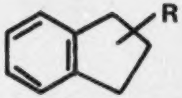
ODOR TYPE	ASSOCIATED STRUCTURES
OILY	ALKYL BENZENES[1] ALKYL INDENES[2]
KEROSENE	ALKYL INDANS[3] ALKYL TETRALINS[4]
SENSATION (FEEL, IRRITATION)	METHYL NAPHTHALENES[5]



(1)



(2)



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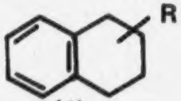
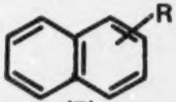


(4)



(5)

Further studies showed that the composition of the aromatic fraction was the same as that isolated from the fuel. The principal source of this odor fraction is, therefore, believed to be in the aromatic fraction of the unburned fuel in the exhaust hydrocarbons.

2. Smoky-Burnt

The chemical species responsible for the smoky-burnt exhaust odor are much more numerous and complex than was the case for the oily-kerosene odor group. The primary species found to be associated with the characteristic odor are listed in Table C-2.

Of the species identified, the greatest contribution to the smoky-burnt odor character appears to be from the higher molecular weight components and those with multi-functional substitution. Feel factors (irritation, pungency) are frequently associated with the lower molecular weight members of a particular chemical class.

Summarized, we find that:

- The smoky odor character is most consistently associated with hydroxy and methoxy indanones with some contributions from methyl and methoxy phenols.
- Burnt odors are associated with furans and alkyl benzaldehydes.
- The oxidized oily character is usually ascribed to alkenones, dienones, hydroxy cyclocarbonyls, and indanones.
- Irritation factors seem most frequently to be associated with the lower molecular weight phenols. Some benzaldehydes and methoxy benzenes may also contribute to this sensation.
- While some unsaturated aldehydes contribute to a portion of the exhaust odor complex, the most abundant exhaust aldehydes do not appear to contribute significantly.
- Neither sulfur nor nitrogen-containing species contribute to the smoky-burnt odor complex. Although such species were observed during portions of the analyses, none were associated with exhaust odors

The major source of the most significant odor contributors in this group appears to be the aromatic portion of the fuel, although some contribution is also seen from the paraffin portion. Confirmation of this observation was obtained with the study of a paraffin fuel (Soltrol 200) where the odor character was seen to change markedly — the odor was not eliminated, however.

Table C-3

ODOR-STRUCTURE CORRELATION
SMOKY-BURNT ODOR COMPLEX

STRUCTURE TYPE	ODOR
ALKENONE	OXIDIZED OILY
DIENONE	OXIDIZED OILY
FURAN	IRRITATION
FURFURAL	BURNT
BENZENES	
METHOXY	SMOKY, PUNGENT
PHENOL	BURNT, IRRITATION
ALDEHYDE	BURNT, PUNGENT
BENZOFURAN	PARTICLE SIZE
INDANONE	SMOKY METALLIC
INDENONE	LEATHERY TARRY BURNT
NAPHTHALDEHYDE	PARTICLE SIZE

APPENDIX D

SAMPLE COLLECTION PROCEDURES

This appendix describes the original silica gel and the new Chromosorb 102 sample collection procedures.

1. SILICA GEL COLLECTION METHOD

Exhaust is sampled from the exhaust manifold by means of a heated particulate filter and heated lines to and from a Teflon diaphragm Dynapump which provides a 0.5 cfm sampling rate. The exhaust sample is passed from the pump through a tube (approximately 2 cm dia. x 10 cm long) containing 25 g of silica gel (Fisher Scientific, 14-20 mesh) which has been acid washed (pH 1-2) and activated at 110°C. A slight odor and hydrocarbon breakthrough is noted after the collection of 720 liters in one hour. A distinct yellow-brown color is observed at the top of the gel trap where the silica is first contacted with the exhaust.

The absorbed sample is extracted from the gel by treating the the silica in the collection tubes successively with 50 mℓ of pentane and 50 mℓ of 10% $MeOH/H_2O$ solution which is 0.01N in H_2SO_4. The aqueous acid methanol extract is reextracted twice with 5 mℓ aliquots of $CHCl_3$. Analysis of the pentane and chloroform extracts suggests that 90% of the organic sample collected is extracted by the pentane. This extract consists primarily of the hydrocarbons. The aqueous acid methanol, on the other hand, is required to complete the extraction of the oxygenated species.

It should also be noted that the greater bulk of the sample collected on the gel trap consists of condensed water vapor and that the amount of organic sample collected bears an inverse relation to the amount of water trapped. No attempt has been made in the course of the present experimentation to control the water accumulation.

2. CHROMOSORB 102 SAMPLE COLLECTION AND ISOLATION

A. Summary

Sufficient sample may be collected from 500 - 1000 liters of exhaust for all of the analyses (odor and analytical) now required using Chromosorb 102 adsorbent traps. The collected exhaust is then isolated by pentane elution.

B. Supplies

Stainless steel collection trap (Figure D-1) - the drawing is to scale (1/1). The Chromosorb is contained between two 100 mesh screens held in slight compression by the coil spring. Complete blueprints are available on request.

Glass funnels - 10 cm diameter with stem dimensions the same as the trap (1/4 in. O.D.) so that they may be close coupled with Teflon tubing.

n-Pentane (Phillips Petroleum, Chromatoquality) - distilled at atmospheric pressure, B.P. 36°C.

Methylene chloride (Fisher Scientific, Spectroquality) - distilled at atmospheric pressure, B.P. 38°C.

Methanol (Fisher Scientific, Spectroquality)

Chromosorb 102 (Johns-Manville, 60/80 mesh)

C. Procedure

1. Chromosorb Preparation

The adsorbent is prewashed as follows: Plug the end of a large 10 cm O.D. glass column with silanized glass wool and transfer into it 150 g of Chromosorb. Wash the Chromosorb in the column successively with 600 mℓ of MeOH, 600 mℓ of methylene chloride, 600 mℓ of n-pentane. Pour these solvents into the column in that order and allow one solvent to drain completely from the column before adding the next solvent. The solvent flow is ca. 5 - 10 mℓ per minute.

The first portions of the solvent wash have a yellow tint and a characteristic odor. The intensity of the color and odor decreases as the prewashing cycle proceeds. The absence of this color and odor should be used as a guide to determine completeness of the prewashing process.

When the prewashing cycle is completed, the adsorbent is left in the column at room temperature for 24 hours to get rid of most of the residual pentane It is then activated at 70°C for 24 hours.

2. Trap Prepration

Ten grams of Chromosorb 102 is weighed out and packed in the stainless steel trap between the wire screens. Glass wool may also be required if the screen mesh is too large. The direction of exhaust flow is marked and the trap weighed to at least ± 10 mg.

3. Exhaust Collection

The trap is connected to the exit side of a Diapump Teflon diaphragm pump with a Swagelok nut and Teflon ferrules. Exhaust (hot, fiber glass filter filtered) is then passed through the trap at about 10 ℓ/min until the desired 500 - 1000 liters have been collected. After collection, the Swagelok fastenings are removed and the trap reweighed.

4. Sample Isolation

The trap is fastened upright on a ring stand above a graduated receiver with the trap inlet side facing down to the receiver. The funnel is then attached to the trap exit end with Teflon tubing.

A separatory funnel or solvent reservoir is positioned just above the funnel and filled with about 10 mℓ of pentane. The solvent is allowed to slowly percolate through the trap. Flow should be about 0.5 mℓ/min. The solvent must be added to what had been the exit end of the trap so that the trapped odor species may be eluted as easily as possible. If the solvent flow is reversed, the trapped species chromatograph on the bed packing with resultant lower recovery.

The first 10 mℓ of pentane effluent is collected and contains all of the total organic extract (TOE).

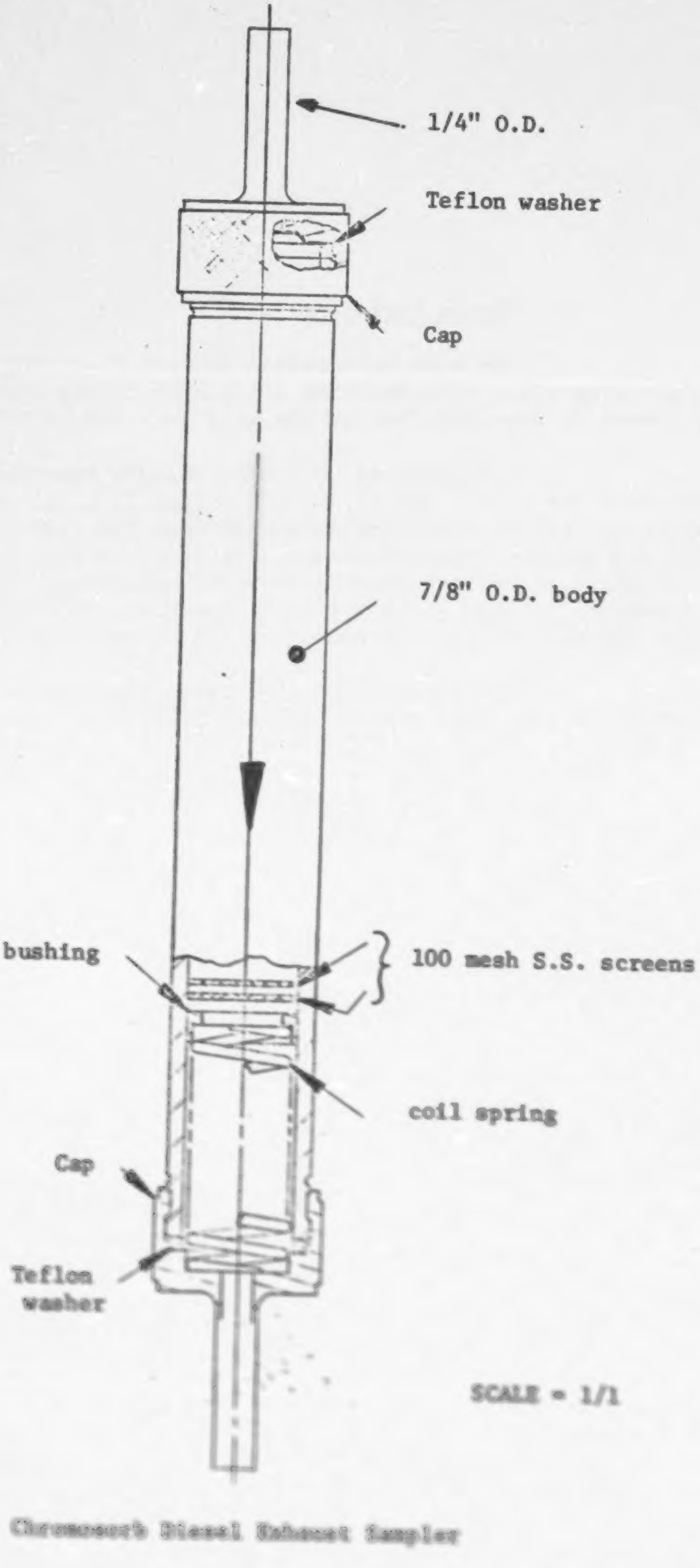

1/4" O.D.
Teflon washer
Cap
7/8" O.D. body
bushing
100 mesh S.S. screens
coil spring
Cap
Teflon washer
SCALE = 1/1

Figure D-1 Chromosorb Diesel Exhaust Sampler

APPENDIX E

LIQUID COLUMN CHROMATOGRAPHY (LCC) PROCEDURES

1. STANDARD PROCEDURE*

In the standard first-stage separation technique, the sample is subjected to silica liquid-column chromatography. The detailed experimental conditions are as follows using the 76,500 liters of exhaust collected in Experiment 25 as an example:

Column Conditions. 1.8 cm ID packed for a length of 20 cm with silica, Grade 950 (Fisher Scientific, 60 to 200 mesh) activated at 110°C for two hours.

Sample Preparation. A small volume (15 ml) or organic condensate extract was mixed with 15 ml silica and transferred to the top of the column.

Elution Scheme. Refer to Table E-1.

Handling of Various Fractions. All fractions were allowed to evaporate overnight at room temperature and the final volume was adjusted to 7.65 ml in each case. Thus, for these examples representative of 76,500ℓ of exhaust.

The fractionation of the sample, along with the elution scheme and qualitative odor is given in Table E-1. Oily-kerosene comes out in fractions 4 or 5 and the smoky-burnt odor character comes out in fraction 10. Since the total Sample 25 had a fuel oil equivalent (FOE) of about 5,000 mg.** about 70% of the mass was in fraction 1, 14% in fraction 5, and only 3% in fraction 10. This procedure was used in preparing the fraction for the identification phase of the smoky-burnt odor studies.

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*Taken from Final report of first year's study, ref. 1.

**Mass of sample as determined from flame ionization detector response based on calibration with fuel oil.

Table E-1

SILICA LCC ELUTION SCHEME AND ODOR OBSERVATIONS FOR SAMPLE 25

Fraction	Solvent	Comment	FOE (mg) [a]	Odor [b]
1	Pentane, 150 ml [c]	Colorless effluent	3, 500	Odorless
2	Pentane, 100 ml	Colorless effluent		
3	Pentane, 100 ml	Colorless effluent		
4	Benzene, 100 ml	The yellow component starts moving down upon addition of benzene; collected effluent was still colorless		
5	Benzene, 100 ml	Greenish yellow effluent	700	Oily, kerosene
6	Benzene, 100 ml	Greenish yellow		
7	$CHCl_3$, 150 ml	Light greenish yellow		
8	5%MeOH/$CHCl_3$, 100 ml	Very light greenish yellow		
9	10% MeOH/$CHCl_3$, 100 ml	Very light greenish yellow		
10	25% MeOH/$CHCl_3$, 100 ml	Brown	150	Smoky-burnt, oily
11	50% MeOH/$CHCl_3$, 100 ml	Brownish yellow		
12	MeOH, 125 ml	Yellow		

a – Fuel oil equivalent; weight of sample based on GC response compared to fuel oil calibration using the FID response from silicone column. Total FOE for Sample 25 ≈5000 mg.

b – Qualitative odor screening observation.

c – The eluted fractions were concentrated to 7.65 ml.

2. MICRO COLUMN PROCEDURE FOR QUANTITATIVE ANALYSIS

A new micro LCC procedure was developed to simplify the analysis and meet the sample handling requirements of the 1000 ℓ exhaust samples collected on the silica gel traps.

The concentrated pentane and chloroform silica gel extracts are fractionated in a micro-column, which consists of a bottom tapered 16 cm piece of 8 mm glass tubing fused to a 6 cm piece of 18 mm glass tubing which serves as solvent reservoir. The column is packed with activated silica Grade 950 (Fisher Scientific, 60-200 mesh) to a height of 12 cm. The volumes of the solvents used for eluting were adjusted correspondingly to establish chromatographic conditions similar to those of our standard LCC fractionation. The elution pattern and odor characteristics are shown in Table E-2.

3. PREPARATIVE ROUTINE PROCEDURE

A. Summary

Diesel exhaust total organic extract (TOE) is separated into the three primary chemical groups (paraffin, aromatic, and oxygenate) by solvent gradient elution on silica gel.

B. Supplies

Chromatographic column - 1.1 cm I.D. x 30 cm with Teflon stopcock.

Graduated test tubes or volumetric flasks - 10 mℓ and 25 mℓ capacity.

Graduated cylinders.

Separatory funnels for use as solvent reservoirs.

n-Pentane (Phillips Petroleum, Chromatoquality) - distilled at atomospheric pressure and representing fraction boiling at 36°C.

Methylene chloride (Fisher Scientific, Spectroquality) - distilled at atmoshperic pressure and representing fraction boiling at 38°C.

Methanol (Fisher Scientific, Spectroquality).

Silanized glass wool.

Teflon tubing - 1/4 inch.

Table E-2

Micro-LCC(a) Fractionation of Gel Trap Samples(b)

Fraction No.	Solvent	Compound Type Eluted and Odor
1	Pentane, 10.0 ml	Aliphatic hydrocarbons; odorless
2	Pentane, 2.5	
3	Pentane, 2.5	
4	Benzene, 11.0	Aromatic hydrocarbons; oily kerosene
5	Benzene, 2.5	
6	Benzene, 2.5	
7	$CHCl_3$, 5.0	
8	10% MeOH/$CHCl_3$, 2.5	
9	10% MeOH/$CHCl_3$, 2.5	
10	10% MeOH/$CHCl_3$, 2.0	Oxygenated compounds; smoky burnt

(a) The micro-column used consists of a short glass tubing of 0.6 cm I.D. and packed with activated silica Grade 950 (Fisher Scientific, 60-200 mesh) to a height of 12.0 cm. The column volume is approximately 2.2 ml.

(b) The pentane and chloroform extracts of the gel traps were concentrated to about 1.0 ml and then applied directly to the top of the column.

Silica Gel (Fisher Scientific Company 60 - 200 mesh, Grade 950) - this adsorbent is activated at 110°C for two hours just prior to use.

C. Procedure

1. Dry pack the chromatographic column, plugged at one end with glass wool, with 6.2 grams of freshly activated silica gel. For properly activated silica gel, a portion weighing 6.3 ± 0.2 g occupies 8 mℓ graduated cylinder.

2. Pour pentane into the solvent reservoir positioned above the column and let the pentane flow into the silica gel bed until the column is homogeneous throughout and free of any break and trapped air bubbles. Gently tapping the column (with a short piece of rubber pressure tubing) aids in tight packing of the column. The total height of the silica bed in this packed column should be 10 cm.

3. As soon as column is ready, allow the pentane level in the column to reach the level of the top of the silica bed. This top portion of the silica bed will be referred to as the origin.

4. Position a 25 mℓ graduated receiver at column end.

5. Quantitatively transfer the 10 mℓ of the TOE directly into the column and maintain solvent flow at 1 mℓ per minute. Add more pentane as required and do not allow column to run dry.*

6. Collect 20 mℓ of pentane effluent. At the end of this collection, the pentane level in the column must be at the origin. Slowly pour 10 mℓ of methylene chloride into the column and collect 4 mℓ more of effluent. This is fraction LCP. (The 24 mℓ of effluent may be made up to 25 mℓ with distilled pentane).

---

* After every change in solvent, make the necessary stopcock adjustment, so that the solvent flow is maintained at 1 mℓ per minute.

7. Replace receiver with a 10 mℓ volumetric flask and collect 10.0 mℓ of methylene chloride effluent. At the end of this collection, solvent level in the column must be at the origin. This is fraction LCA. (Carefully, control the last portion of methylene chloride added into the column to avoid exceeding the required amount).

8. Replace receiver with another 10.0 mℓ volumetric flask and pour 10 mℓ of 50% methanol/methylene chloride into the column. Collect 10.0 mℓ of effluent. This is fraction LCO.

This procedure can be represented schematically as shown in Figure E-1. It has been possible to automate this procedure with pumps, closed columns, detectors, etc., but the overall efficiency is not especially improved. The manual procedure is quite satisfactory for the analytical needs and, with a small amount of practice, simple and efficient to use.

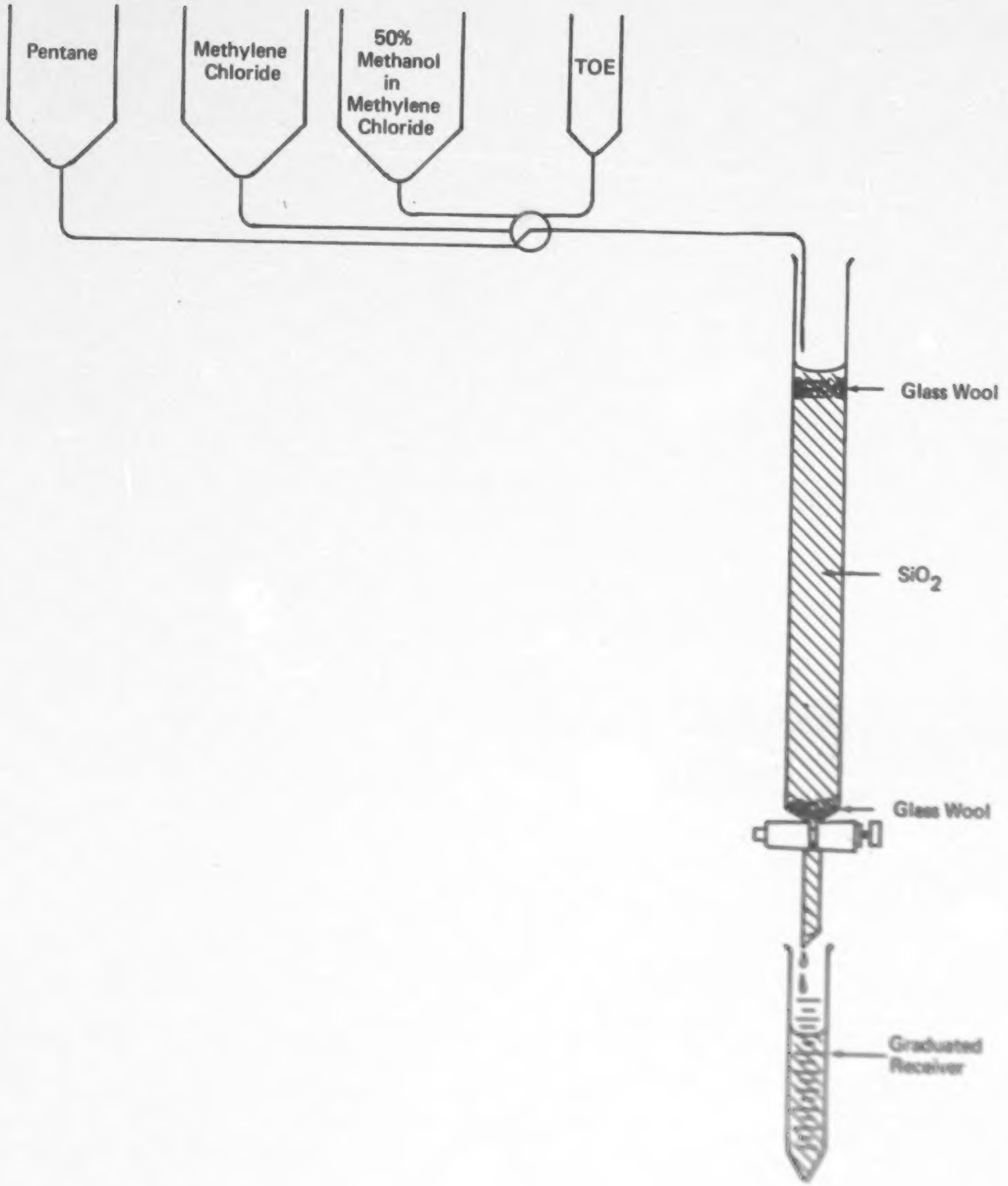

Pentane
Methylene Chloride
50% Methanol in Methylene Chloride
TOE
Glass Wool
SiO_2
Glass Wool
Graduated Receiver

Figure E-1 Preparative LCC Schematic

APPENDIX F

GAS CHROMATOGRAPHIC MASS ANALYSIS OF EXHAUST SAMPLES

Most of the relationships developed between composition and odor have been based on the mass (weight) of the exhaust sample. A gas chromatography simple procedure was developed to provide data on the total mass of the sample present in the solutions of the various total exhaust organic extract (TOE) and liquid chromatography fractions (LCA, LCO).

1. PROCEDURE

Equipment - Temperature programmable gas chromatograph with FID detector (P-E 900).

Column - 1/8" O.D. x 1½ ft stainless steel packed with 10% OV-1 on 100/120 mesh Gas Chrom Q.

Temperature Program - Initial isothermal operation at room temperature for three minutes after sample injection to allow solvent elution - then ballistic heating to 250°C in three minutes. A typical chromatogram is shown in Figure F-1.

Calibration - Achieved by measuring the area FID response from a 1% or 0.1% solution of diesel fuel in pentant. The mass in a sample thus related to fuel is measured as a fuel oil equivalent (FOE).

2. RESULTS

The reproducibility of the procedure can be seen from the data in Table F-1 which was obtained by repeated analysis of the same samples on the dates shown.

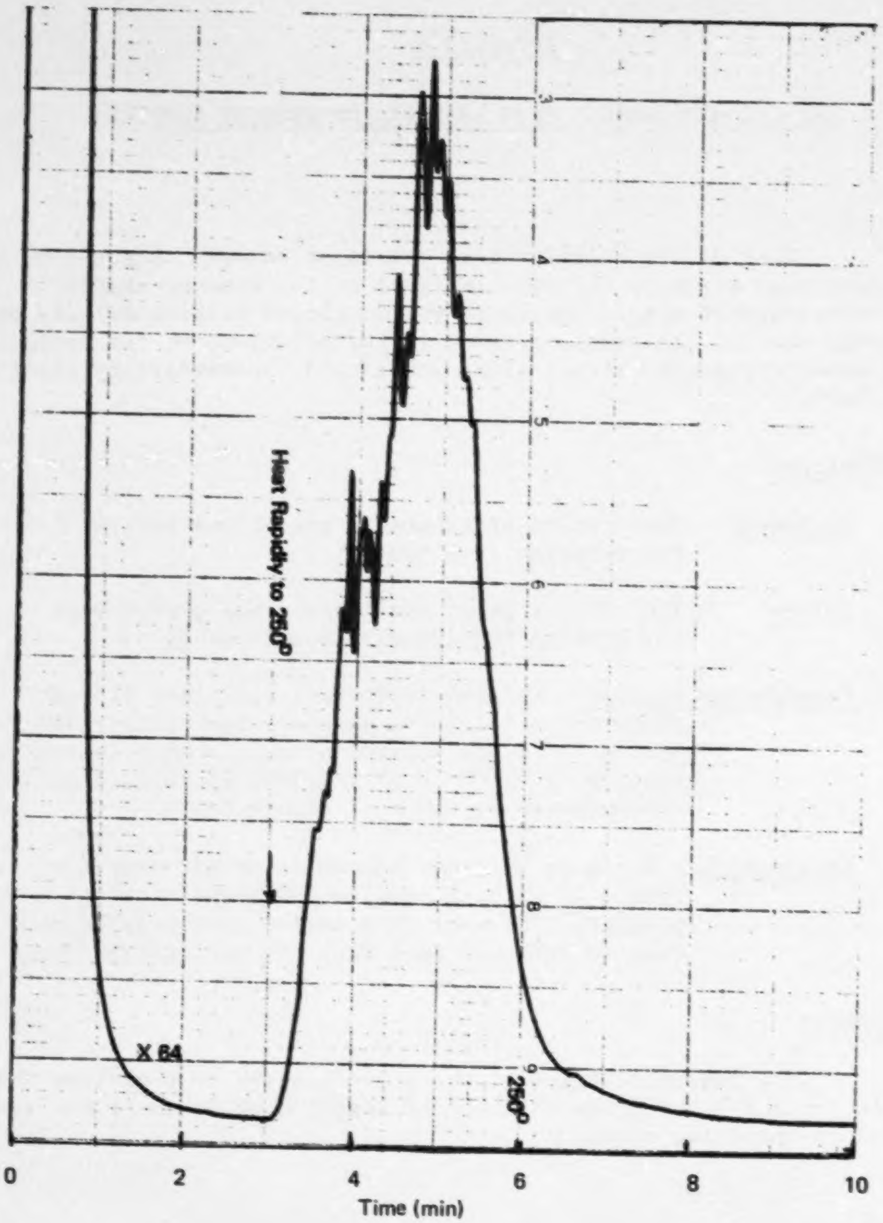


FIGURE F1 TOTAL ORGANIC MASS GAS CHROMATOGRAPHIC ANALYSIS OF AN LCO EXHAUST SAMPLE

Table F-1

Reproducibility of Total Organic GC Method

Date	Fuel Oil Response (sq. in/μg)	--------Total Organics[a] Observed in---------		
		LCP	LCA	LCO
12/18/70	27.1	50.4	9.1	1.40
12/23/70	30.7	45.7	8.0	1.40
12/29/70	26.6	52.8	11.1	1.34
1/5/71	27.1	49.4	8.6	1.05
1/14/71	24.5	-	11.5	1.24
Average	27.2±3.5	49.6±4.0	9.7±1.8	1.29±0.24

a. μg/ℓ as FOE values

APPENDIX G

MASS SPECTROMETRIC ANALYSIS OF DIESEL EXHAUST

ODOR FRACTIONS

Computer programs have been developed for the detailed composition analysis of the LCA and LCO oily-kerosene and smoky-burnt odor fractions isolated from diesel exhaust by the liquid chromatography procedures. A complete Fortran program listing is available from our laboratories on request. The basic characteristics of each program are described briefly in this appendix.

1. AROMATICS--OILY-KEROSENE FRACTION

The procedure for the LCA fraction is a modification of the usual matrix analysis of aromatic fractions conducted by the petroleum industry. The version developed by the Mobil Research and Development Corporation was kindly supplied to us for our studies. The program was modified to enable us to process data on our laboratory Hewlett-Packard 2116B computer.

The input requirements are a listing of the unit mass peak height intensities from m/e 80 obtained from a low resolution ($m/\Delta m$ = 500) mass spectrum of the LCA fraction. A typical input is shown in Table G-1.

The resultant final analysis from that set of data is given in Table G-2. The exhaust and fuel samples from No. 1 fuel do not normally have a significant amount of the acenaphthene and phenanthrene classes, but these classes are more significant in higher boiling fuels. Data in this form provide a means for determining the indan/tetralin concentration in the exhaust related to the kerosene odor.

2. OXYGENATES--SMOKY-BURNT FRACTION

A procedure, similar in concept to that used for the aromatics fraction, has been developed for comparative analysis of the oxygenate (LCO) odor fraction. The method is based on a Fortran program analysis of the high resolution mass spectrum of the LCO sample.

TABLE G-1

INPUT DATA FOR AROMATICS MATRIX ANALYSIS

Listing of observed peak heigh intensities, in arbitrary units, listed in order of increasing mass.

```
m/e 80
     0     0     0     0     0     0     0     0     0     0
     0   360   189   480   510   240   150   210    87   453
   180  1860   747   156   178   153    81   117   300   108
   123   168   336   304   261  1008   329   120    54   102
    60    63    54   168   111  2028   429   531   294  1866
   477    96    51    62    24    62   299   738  2802   915
   270   633   309  1044   888   198    39    66    59   750
   238  4950  3720   717   201   714   336   489   420   102
   156   240   807   891   711  2550  4350   742   168   657
   306   369   330   114    59   348   166   546   639   516
  1555   339   135   462   249   147   225    63    84    59
    41   155   305   114   210    84   105   156   177    57
    75    26    24    21    20    30    74    27    42    30
    58    36    84    15    29     6     5    24     6     6
    25     4     7     3     9     5    12     2     6     1
     1     1     2     1     3     2     1     1     2     1
     2     0     1     0     0     0     0     0     0     1
                                                               m/e 249
```

TABLE G-2

AROMATICS COMPOSITION ANALYSIS OF AN OILY-KEROSENE LCA ODOR FRACTION

Species	Composition
Alkylbenzenes	24.7
Tetralins, Indans, Indenes	13.4
Naphthalenes	63.1
Acenaphthenes, etc.	-.4
Phenanthrenes, etc.	-.7
	100.0

In the analysis a complete high resolution spectrum ($m/\Delta m$ = 10,000) is first obtained on the sample. The first and last page of the output from a typical sample is listed in Table G-3. The full spectrum typically contains data on 500 - 1000 spectral lines. This spectrum contains all of the basic mass (DET), R+DB value (DB), and composition (C12/13 H O). The analysis procedure takes advantage of all of this chemically resolved data and that desirable and undesirable data (hydrocarbon interferences, fragmentation, isotopes) are resolved and can be easily separated.

This output is also provided on punched cards as input for the analysis procedure. A Fortran IV program is written for use on an IBM 360/65 computer. The data from the entire sample is then searched, and the program is instructed to list all of the desired chemistry. In arriving at criteria and a format for listing the data, we utilized as much of the previously determined specific chemical identification data as possible. We also chose groupings which satisfied our initial feeling of the odor significance of certain chemical classes. We have found it convenient to discuss the odor significant chemical classes in terms of their R+DB (rings plus double bonds--a representation of chemical unsaturation) values and have shown that the species in a particular R+DB class have primarily one type of chemistry. For instance, R+DB 2 with 1 oxygen is primarily unsaturated aldehydes or ketones, R+DB 4 with 2 oxygens is primarily methoxy and hydroxy substituted phenols.

Further, we have determined that unsaturated aldehydes are more closely related to oxidized oily odors than those with 2 oxygens. Similarly, indanols and indanones (R+DB 5 and 6) with 2 oxygens are more odor significant than those with 1 oxygen for the burnt odor character.

A review of the meaning of R+DB, as given in the last final report (ref. 3) is appropriate at this point. One of the most useful first interpretative aids in restricting the possible structural assignments are the R+DB values listed in the appendix tables. R+DB stands for "rings plus double bonds" and is an interpretive aid taken from McLafferty's treatment of mass spectral data. (ref. 4) Values of R+DB are basically arrived at by a simple analysis of the degree of unsaturation in a molecule with a particular composition. For species containing only carbon, hydrogen, and oxygen, the values are arrived at numerically from the formula

$$\text{R+DB} = \text{No. C atoms} - \tfrac{1}{2}(\text{No. H. atoms}) + 1$$

Several examples will serve to demonstrate the utility of the values:

for an n-paraffin C_6H_{14}

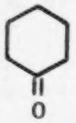
R+DB = 6 - 7 + 1 = 0; i.e., the n-paraffin has no rings nor double bonds

for a hexenone $C_6H_{10}O$

R+DB = 6 - 7 + 1 = 2; fitting a structure

CH_3-CH_2-CH_2-CH = CH-CHO

Cyclohexanone also satisfies the R+DB criteria having one ring and one double bond.



The Fortran program has been written to organize all of the data by R+DB class and number of oxygen atoms and also includes the following exclusion criteria in order to minimize information unique to the mass spectrometric fragmentation process, and match the identification data:

1) Only even mass ions are considered (fragment ions have too many origins).

2) Only ions above mass 94 are searched (no odorous species were found below this MW).

3) No ^{13}C isotope peaks are included.

4) Peaks with large composition computation error (greater than 0.002 amu) are excluded.

5) Ions without oxygen (hydrocarbons) are excluded.

6) An ion in a particular R+DB class must have at least the following number of carbon atoms

R+DB	Lower C Limit
0	5
1	5
2	6
3	4
4	6
5	7
6	8
7	9
8	10

A complete listing of the output obtained from the full spectral data is given in Table G-4. A listing is obtained within an R+DB and oxygen restriction of all of the observed species including their relative abundance (HGT, normalized to a base of 1000 for the total data set, molecular weight (DET.MASS), and composition (^{12}C,H,O). A total sum of each R+DB/oxygen group is thus also listed (SUM HGT). From such an analysis for all R+DB classes, the final analysis matrix is then assembled as shown in Table G-5.

The data in this table has been normalized to total 100% and therefore represents the mass spectrometric abundance of any particular R+DB/oxygen combination. These abundances have not yet been adjusted for the relative differences inherent in the parent ion intensity due to differences in fragmentation patterns between chemical classes. An approximation of the relative amount of any particular combination of chemical classes can be computed from the product of the summed (or individual) percentages and the concentration of total sample (FOE value) in mg/Kℓ. These values can then be used for odor correlations.

Presently we feel that the oxidized oily character note of these odor fractions should be due to the unsaturated aldehydes and furans represented in the R+DB $2/O_1$, R+DB $3/O_1$ and O_2 classes. Some portion of the smoky character should be due to the phenols, acetophenones, and indanones in R+DB $4,5,6/O_2$, and perhaps some irritation is due to the simpler phenols in R+DB $4/O_1$ class. At the present time we do not feel that the chemistry represented in R+DB classes 1, 7, and 8 or the O_3 classes contribute significantly to the odor from most operating conditions; however, they may become important under some test conditions.

Table G-3

High Resolution Mass Spectrum

```
                    SERIAL NUMBER    829
         CHROM - 33-1A  LCC 50(MEOH  PP 9-27 EXP 11./

             MAXHET= 4     C-13= 1     C-16= 4
INT(ESTM)     DIST       DETM       CALC      ERROR      DB      X    C12/13   H  O

      19     0.5377   70.03146   ***  (No Composition Assigned for C, H, O)

      96     0.5487   70.04116   70.04186 -0.71     2.00     2      4/0    6  1

     337     0.5889   70.07662   70.07825 -1.63     1.00     0      5/0   10  0
       6     1.1070   70.53448   ***
       7     1.6271   70.99561   ***

      18     1.6470   71.01328   71.01330 -0.02     2.50     3      3/0    3  2
      18     1.6674   71.03140   ***
      13     1.6772   71.04011   ***

     204     1.6875   71.04926   71.04969 -0.43     1.50     1      4/0    7  1

     228     1.7278   71.08507   71.08608 -1.01     0.50    -1      5/0   11  0
       3     2.6815   71.93507   ***

       3     2.7772   72.02064   72.02113 -0.49     2.00     2      3/0    4  2
       2     2.7856   72.02815   ***
      53     2.8015   72.04238   ***

     127     2.8171   72.05633   72.05751 -1.18     1.00     0      4/0    8  1

       9     2.8533   72.08872   72.08943 -0.71     0.50    -1      4/1   11  0

      40     3.8786   73.00915   73.00783  1.33     6.50    11      6/0    1  0
      25     3.9213   73.04761   ***

       3     3.9352   73.06013   73.06087 -0.74     1.00     0      3/1    8  1

      38     3.9403   73.06473   73.06534 -0.61     0.50    -1      4/0    9  1
```

Table G-3 cont........

4	107.6402	196.18192	196.18271	-0.80	2.00	2	13/0	24	1
3	108.2870	197.13487	197.13303	1.84	7.50	13	15/0	17	0
2	108.3251	197.19107	197.19054	0.54	1.50	1	13/0	25	1
3	108.9697	198.14322	198.14085	2.37	7.00	12	15/0	18	0
2	109.6495	199.14984	199.14868	1.16	6.50	11	15/0	19	0
6	110.3031	200.12007	200.12011	-0.04	7.00	12	14/0	16	1
5	110.9797	201.12695	201.12794	-0.99	6.50	11	14/0	17	1
13	111.6557	202.13546	202.13576	-0.30	6.00	10	14/0	18	1
5	112.2975	203.09529	***						
3	112.3281	203.14111	203.14359	-2.48	5.50	9	14/0	19	1
			203.13912	1.99	6.00	10	13/1	18	1
2	112.9773	204.11442	204.11503	-0.61	6.00	10	13/0	16	2
7	113.0012	204.15030	204.15141	-1.12	5.00	8	14/0	20	1
3	113.0264	204.18813	204.18780	0.33	4.00	6	15/0	24	0
3	113.6717	205.15802	205.15924	-1.22	4.50	7	14/0	21	1
10	114.3415	206.16688	206.16706	-0.18	4.00	6	14/0	22	1
6	115.0081	207.17339	207.17489	-1.50	3.50	5	14/0	23	1
8	115.6747	208.18234	208.18271	-0.37	3.00	4	14/0	24	1
2	117.0009	210.19695	210.19836	-1.42	2.00	2	14/0	26	1
1	119.5750	214.13444	214.13576	-1.33	7.00	12	15/0	18	1
3	120.8838	216.15027	216.15141	-1.15	6.00	10	15/0	20	1
5	121.5038	217.10849	***						

Table G-4

R+DB Analysis of an LCO Smoky-Burnt Odor Fraction

```
 SERIAL NUMBER    829
          CHROM - 33-1A  LCC 5C(MECH  PP 9-27 FXP 11./


ANALYSIS FOR DB=   0

          HGT   DET. MASS          C12  H  O



SUM HGT =     0/1000    NUMBER OF CXYGENS =    1






SUM HGT =     0/1000    NUMBER OF CXYGENS =    2






SUM HGT =     0/1000    NUMBER OF CXYGENS =    3
```

```
SERIAL NUMBER     829
          CHROM - 33-1A  LCC 50(MECH  PP 9-27 EXP 11./


ANALYSIS FOR DB=   1

          HGT    DET. MASS              C12  H  O


          12    100.08688               6 12  1
           0    142.13385               9 18  1

SUM HGT =     12/1000     NUMBER OF OXYGENS =    1



SUM HGT =      0/1000     NUMBER OF OXYGENS =    2



SUM HGT =      0/1000     NUMBER OF OXYGENS =    3
```

```
SERIAL NUMBER     829
          CHROM - 33-1A  LCC 50(MECH  PP 9-27 EXP 11./

ANALYSIS FOR DB=    2

               HGT    DET. MASS           C12  H  O


                85     98.07167             6 10  1
                29    112.C8760             7 12  1
                19    126.10295             8 14  1
                10    140.11863             9 16  1
                 4    154.13436            10 18  1
                 1    168.15037            11 20  1
                 1    182.16655            12 22  1
                 1    196.18192            13 24  1
                 0    210.19695            14 26  1

SUM HGT =    150/1000     NUMBER OF OXYGENS =     1




                 5    114.06759             6 10  2
                 1    128.08238             7 12  2
                 2    142.09859             8 14  2

SUM HGT =      8/1000     NUMBER OF OXYGENS =     2




SUM HGT =      0/1000     NUMBER OF OXYGENS =     3
```

```
      SERIAL NUMBER      829
                 CHROM - 33-1A  LCC 5C(MECH  PP 9-27 EXP 11./

     ANALYSIS FOR DB=    3

                    HGT     DET. MASS             C12  H  O


                    50      96.05617               6  8  1
                    25     110.07166               7 10  1
                    22     124.08696               8 12  1
                    10     138.10308               9 14  1
                     7     152.11942              10 16  1
                     6     166.13447              11 18  1
                     5     180.15070              12 20  1
                     4     194.16581              13 22  1
                     3     208.18234              14 24  1
                     2     222.19783              15 26  1

     SUM HGT =     134/1000       NUMBER OF OXYGENS =      1






                    10      98.03619               5  6  2
                     5     112.05168               6  8  2
                     7     126.06641               7 10  2
                     2     140.08263               8 12  2
                     1     154.09831               9 14  2
                     0     168.11423              10 16  2

     SUM HGT =      25/1000       NUMBER OF OXYGENS =      2






     SUM HGT =       0/1000       NUMBER OF OXYGENS =      3
```

```
SERIAL NUMBER     829
              CHROM - 33-1A  LCC 50(MEOH  PP 9-27 EXP 11./


ANALYSIS FOR DB=    4

               HGT    DET. MASS          C12  H  O


               15     94.04116             6  6  1
               22    108.05606             7  8  1
               22    122.07163             8 10  1
                9    136.08776             9 12  1
                8    150.10330            10 14  1
                8    164.11914            11 16  1
                5    178.13522            12 18  1
                4    192.15052            13 20  1
                4    206.16688            14 22  1
                2    220.18204            15 24  1

SUM HGT =     99/1000     NUMBER OF OXYGENS =     1






                8    110.03585             6  6  2
                4    124.05119             7  8  2
                3    138.06709             8 10  2
                3    152.08322             9 12  2
                2    166.09842            10 14  2
                1    180.11486            11 16  2

SUM HGT =     21/1000     NUMBER OF OXYGENS =     2





                1    126.03012             6  6  3

SUM HGT =      1/1000     NUMBER OF CXYGENS =     3
```

```
SERIAL NUMBER    829
                  CHROM - 33-1A  LCC 50(MECH  PP 9-27 EXP 11./


ANALYSIS FOR DB=    5

                  HGT    DET. MASS          C12  H  O


                   39    120.05583            8  8  1
                   51    134.07126            9 10  1
                   33    148.08781           10 12  1
                   16    162.10406           11 14  1
                    9    176.11936           12 16  1
                    5    190.13507           13 18  1
                    3    204.15030           14 20  1

SUM HGT =    156/1000     NUMBER OF OXYGENS =     1





                   13    122.03626            7  6  2
                    4    136.05155            8  8  2
                    9    150.06747            9 10  2
                    5    164.08263           10 12  2
                    1    178.09902           11 14  2

SUM HGT =     32/1000     NUMBER OF OXYGENS =     2





                    0    138.03086            7  6  3
                    0    166.06454            9 10  3

SUM HGT =      0/1000     NUMBER OF OXYGENS =     3
```

```
SERIAL NUMBER    829
          CHROM - 33-1A  LCC 50(MECH  PP 9-27 EXP 11./


ANALYSIS FOR DB=   6

               HGT    DET. MASS          C12  H  O


                20    118.04192            8  6  1
                23    132.05671            9  8  1
                36    146.07182           10 10  1
                25    160.08751           11 12  1
                13    174.10318           12 14  1
                10    188.11959           13 16  1
                 6    202.13546           14 18  1
                 1    216.15027           15 20  1

SUM HGT =   134/1000    NUMBER CF CXYGENS =    1






                 6    134.03579            8  6  2
                10    148.05171            9  8  2
                11    162.06791           10 10  2
                 5    176.08253           11 12  2
                 1    190.09798           12 14  2
                 0    204.11442           13 16  2

SUM HGT =    33/1000    NUMBER OF OXYGENS =    2






                 5    150.03010            8  6  3
                 2    164.04761            9  8  3

SUM HGT =     7/1000    NUMBER CF CXYGENS =    3
```

```
SERIAL NUMBER     829
            CHROM - 33-1A  LCC 50(MEOH   PP 9-27 EXP 11./


ANALYSIS FOR DB=    7

                 HGT    DET. MASS          C12  H  O


                   3    130.04132            9  6  1
                   7    144.05714           10  8  1
                  12    158.07230           11 10  1
                  11    172.08738           12 12  1
                   5    186.10351           13 14  1
                   2    200.12007           14 16  1
                   0    214.13444           15 18  1

SUM HGT =      40/1000      NUMBER OF OXYGENS =      1






                   6    146.03622            9  6  2
                   8    160.05224           10  8  2
                   3    174.06781           11 10  2
                   0    188.08240           12 12  2

SUM HGT =      17/1000      NUMBER OF OXYGENS =      2






                   2    162.03177            9  6  3
                   2    176.04667           10  8  3

SUM HGT =       4/1000      NUMBER OF OXYGENS =      3
```

```
 SERIAL NUMBER    829
              CHROM - 33-1A  LCC 50(MECH  PP 9-27 EXP 11./


ANALYSIS FOR DB=   8

              HGT    DET. MASS          C12  H  O


               21    156.05671           11  8  1
               23    170.07220           12 10  1
                6    184.08764           13 12  1

SUM HGT =    50/1000     NUMBER OF OXYGENS =    1









                2    158.03632           10  6  2
                4    172.05179           11  8  2
                5    186.06853           12 10  2

SUM HGT =    11/1000     NUMBER OF OXYGENS =    2










SUM HGT =     0/1000     NUMBER OF OXYGENS =    3
```

TABLE G-5

R+DB MATRIX REPRESENTATION OF CHROM 33 LCO FRACTION

R+DB	O_1	O_2	O_3
0	0	0	0
1	1	0	0
2	15	8	0
3	13	2	0
4	10	2	0
5	16	3	0
6	13	3	1
7	4	2	0
8	5	1	0